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MINERALOGY, GEOCHEMISTRY AND STRATIGRAPHY OF THE BESA RIVER SHALE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY

by

ERNEST EDWARD PELZER, B. Sc.,

EDMONTON, ALBERTA

April, 1965

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Mineralogy, Geochemistry and Stratigraphy of the Besa River Shale", submitted by Ernest Edward Pelzer, B.Sc., in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

April, 1965

"I have long discovered that geologists never read each other's works, and that the only object in writing a book is a proof of earnestness, and that you do not form your opinions without undergoing labour of some kind"

- Charles Darwin.

ABSTRACT

The Besa River Formation of northeast British Columbia is a black shale of Devono-Mississippian age. The formation varies in thickness from a minimum of 1,000 ft. to a maximum of over 7,000 ft. Because of lithologic uniformity and sparse faunal content, subdivision of the formation by conventional methods is not possible.

Results of X-ray diffraction and X-ray fluorescence studies are utilized to provide mineralogical and geochemical criteria for correlation within the Besa River Formation and from the formation to the equivalent shelf deposits to the east. The mineralogical and geochemical criteria permit subdivision of the Besa River Shale and its equivalents to the level of Series in eleven of the thirteen control points utilized in the study, and to the level of Stage in seven of the thirteen control points.

The correlations presented indicate that the thin Besa River Shale sections of the Northern Rockies are fondothemic in character, and represent continuous deposition in deep water throughout a period extending from Givetian to Chesterian time. Thicker Besa River sections to the east and south represent the clinothem, with maximum thickness of each stratigraphic interval occurring at the upper edge of the clinoform. Gradual westward progradation of the clinoform with time is observed. The undathem is represented by barrier reef complexes, blanket shelf carbonates and interbedded calcareous shales and limestones.

Thick assemblages of volcanics, cherts and greywackes to the west of the Rocky Mountain Trench represent eugeosynclinal conditions. Deposits of this character are sporadic in occurrence and related to local areas of active vulcanism. Lack of evidence for Devono-Mississippian deposition over much of the present Cordilleran area may be due to the presence of unrecognized very thin and non-fossiliferous deposits similar to those of the Northern Rockies.

Petrographic studies and relationship of mineral facies to basin topography suggest that a very high proportion of the quartz fraction of the Besa River Shale is of organic or chemical origin rather than detrital. Evidence suggests a southeasterly provenance for the clay minerals. The difficulties encountered in visualizing transport of these clays across the Devonian evaporite basins of southern Alberta and Saskatchewan leads to the suggestion that these minerals were either derived from volcanic ash and moved to the shelf margins, or that they were generated within the shale basin from dilute solutions of their constituents.

The problem of mode of origin of thin radioactive black shales is examined. It is shown that depth of water is not a critical factor in their formation, since they occur on both undaform and clinoform and are still recognizable for some distance into the fondoform. The unique position of these black radioactive shales as the basal phase of a shale transgression across shelf carbonates is noted. In all cases considered, the shelf carbonates show evidence of restriction or sill development, and thus the hypothesis is advanced that resorption of evaporites by the transgressing seas produces density stratification with a dense and highly saline bottom layer overlain by waters of near-normal salinity. The basinward movement of the dense saline bottom layer provides the physico-chemical environment required to explain the unique mineralogy and geochemistry of the shales, and also explains the occurrence of this type of shale over a wide range of water depths.

Finally, it is suggested that studies of this nature have potential economic application in the localization of undathem edges such as the shale-out margins of the Slave Point-Presqu'ile complex and of the Debolt Formation. Mineralogical and geochemical zonation of thick shale units may also have application in the solution of structural problems in foothills drilling.

ACKNOWLEDGEMENTS

Many individuals and institutions have contributed to this study. In terms of financial support, the writer is indebted to the University of Alberta for an Intersession Bursary and to the Consolidated Mining and Smelting Co. for assistance through a Graduate Fellowship. The California Standard Company provided support for three weeks of field studies.

The writer also wishes to thank Canadian Stratigraphic Services, Shell Oil of Canada, The California Standard Co., and the Geological Survey of Canada for the loan of well samples and for permission to remove the cuttings required for this study.

Acknowledgement is made to the National Research Council which, by means of Operating Grant A-1042, has provided support for the X-ray diffraction and fluorescence aspects of the study.

Drs. F. A. Campbell, C. R. Stelck and J. F. Lerbekmo provided supervision for the project and were most helpful with their advice and encouragement and with critical reading of the manuscript.

Drs. E. W. Bamber, R. M. Procter and G. C. Taylor of the Geological Survey of Canada provided samples of the Besa River Shale type section and assistance in the examination and discussion of field sections.

Dr. R. Green of the Alberta Research Council identified ostracods found in the course of sample examination, and Dr. A. C. Lenz, now of The University of Western Ontario arranged identification of a goniatite through Drs. M. House and W. H. Ramsbottom.

Dr. D. Simpson of the Computer Science Faculty, University of Alberta, assisted in the development of a computer program for correction of Al_2O_3 and SiO_2 analyses for mass absorption effects.

The techniques employed in this investigation were developed upon a

foundation of previous studies of shale mineralogy and geochemistry at the Department of Geology of the University of Alberta. The writer has drawn freely upon this work with regard to both information and inspiration, and wishes to acknowledge in particular the benefits derived directly from the work of Drs. F. A. Campbell and J. F. Lerbekmo (1), Drs. F. A. Campbell and G. D. Williams (2), and W. R. Maiklem (3).

(1) Campbell, F. A. and Lerbekmo, J. F.: Mineralogic and chemical variations between Upper Cretaceous continental Belly River shales and marine Wapiabi shales in western Alberta, Canada; Sedimentology, 2 (1963), p. 215.

(2) Campbell, F. A. and Williams, G. D.: Chemical composition of shales of Mannville Group (Lower Cretaceous) of central Alberta, Canada; Bull. Amer. Assoc. Petrol. Geol., Vol. 49 p. 81.

(3) Maiklem, W. R.: Clay minerals from some Upper Cretaceous bentonites, southwestern Alberta; M.Sc. Thesis, Dept. of Geology, University of Alberta.

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CHAPTER ONE

INTRODUCTION

A. Statement of Problem

The Besa River Formation was defined by Kidd (1962, 1964) as:

"the thick black shale sequence which is present in northeast British Columbia foothills and mountains, lying between Mississippian cherty limestones and Middle Devonian carbonates".

The type section designated by Kidd is situated in the front ranges of the Rocky Mountains, some four miles north of the Muskwa River, at 57° 56' 30"N, 123° 43' 00"W. At the type section the basal portion of the formation is not exposed, and the thickness of 3000 feet estimated by Kidd included only 2700 feet of measured section.

The age range of the formation in the vicinity of the type section is given as:

"Upper Devonian and possibly older, to Kinderhook and possibly younger".

Exploratory drilling and field investigations northward from the Besa River type section to and beyond the 60th parallel have revealed extreme stratigraphic complexity within the entire Upper Paleozoic. This complexity arises because of major thickness and facies variations, the extent of which may be gauged from Table 1, which illustrates major lithologic units, their thickness, approximate correlations and the formational nomenclature which has been advanced for the area by Sutherland (1958), Patton (1958), Belyea and McLaren (1962), Gray and Kasube (1963) and Harker (1963).

Perusal of Table 1 shows that the post-Middle Devonian section of the Paleozoic is predominantly clastic and ranges in thickness from some 10,000 feet near the 60th parallel to about 1600 feet in the Summit Lake area, only 80 miles to the south. The Fort Nelson area to the east and the type section of the Besa River, further to the south, both display intermediate thicknesses. Major facies

FORMATION NOMENCLATURE

BESA RIVER TYPE AREA	SUMMIT LAKE AREA	FORT NELSON AREA	SOUTHEAST YUKON	STAGE	PERIOD
	Fantasque Chert 50'		Fantasque Chert, Silt 200'+		PERMIAN
	? ? Unnamed Silt, Sh., Ss. 500'		Mattson Ss. 3100'-4700'		PENNSYLVANIAN
	? — ?			CHEST.	MISSISSIPPIAN
Prophet Ls., Chert 700'		Debolt Ls. 700'	Etanda Sh., Ss. 2000'+ / Flett Ls. 1500' / Clausen Sh. 500'	MERAM. / OSAG.	MISSISSIPPIAN
Besa River Shale 3000'	Besa River Shale 1000'	Shunda - Pekisko Ls., Sh. 600'	Yohin Ss. 600'	KIND.	MISSISSIPPIAN
		Banff Sh. 600'			
		Exshaw Sh. 50' / Kotcho Sh. 250' / Tetcho Ls. 100' / Trout R. Sh. 100'	Unnamed Sh. 2000-3000'	FAMENNIAN	DEVONIAN
		Kakisa Ls. 100' / Redknife - Ft. Simpson Sh. 2000'		FRASNIAN	DEVONIAN
		Horn River Sh. 700' / Muskwa Sh. 50' / Slave Point - Presqu'ile Ls., Dol. 900' / Keg River Dol. 250'+		GIVETIAN	DEVONIAN
"Lower Elk Point" Ls., Dol.	"Lower Elk Point" Ls., Dol.	Chinchaga Dol.	Nahanni	EIFELIAN	DEVONIAN

TABLE 1

changes include the westward shaleout of the Slave Point-Presqu'ile carbonate complex and a similar westward shaleout of the Upper Mississippian carbonates.

In the light of the foregoing gross relationships, the purposes of this study of Besa River stratigraphy may now be outlined as:

1. To evaluate in a more precise fashion the relationship of the Besa River to its lateral equivalents.
2. To attempt to define more fully the age range of the formation.
3. To outline the area of applicability of the formational nomenclature.
4. To determine what paleogeographic and/or tectonic significance can be deduced from the thickness changes of the Besa River and from the facies changes into the lateral equivalents.

B. Method of Investigation

The conventional approach to a problem in shale stratigraphy would favour faunal or palynological studies. Previous experience had discouraged such an approach in this instance because of paucity of fauna and because of progressive westward destruction of palynomorphs through low grade metamorphism. In consequence, the approach used has been that of a comprehensive study of the mineralogy and geochemistry by means of X-ray diffraction and fluorescence methods.

Although the primary purpose of the study has been to provide correlation aids in the form of mineralogical and geochemical markers, additional dividends have accrued in the form of information on mineral and geochemical facies and their paleogeographic locale within the basin framework.

A total of thirteen control points was utilized, selected so as to constitute three cross-sections which interlock to form a closed loop. This procedure minimizes the possibility of miscorrelations inasmuch as any odd number of miscorrelations on a given marker will produce a mis-tie within the loop.

Ten of the control points selected for study are subsurface and three are

measured surface exposures. Number, name and location of each control point is given in Table II, and the position of the control points and of the three interlocking sections is illustrated on the Index Map, Figure 1.

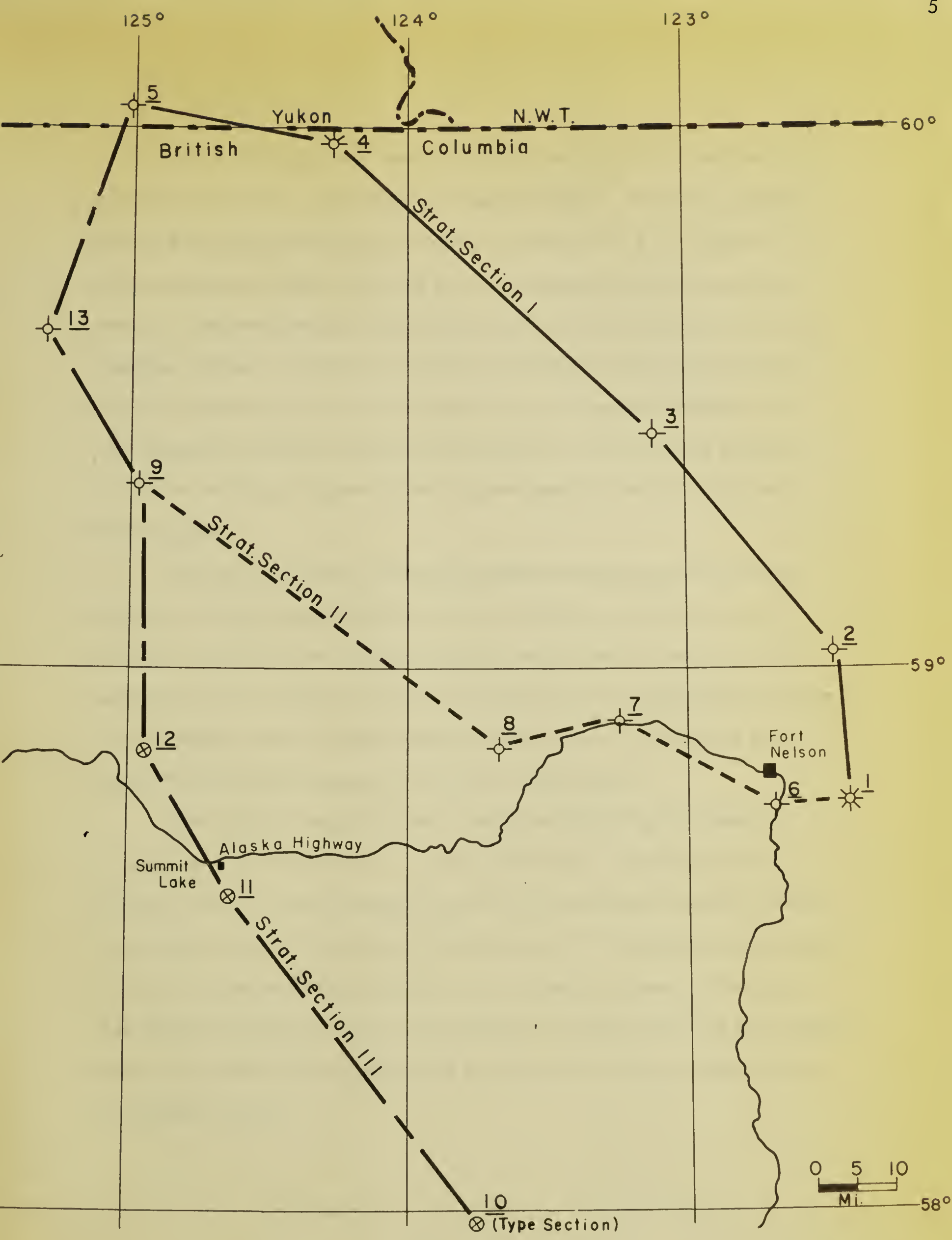
TABLE II

NAMES AND LOCATIONS OF CONTROL POINTS

(Latitudes and longitudes approximate)

1. Gulf States - Imp. Clarke Lk. #2; C-94-L-94-J-9: 58° 45'N, 122° 25'W.
2. Pan-Am. Snake River #A-1; C-28-D-94-0-1: 59° 02'N, 122° 29'W.
3. Pan-Am. Deer Lake #A-1; a-90-I-94-0-6: 59° 26'N, 123° 07'W.
4. Pan-Am. Beaver River #A-1; b-63-K-94-N-16: 59° 58'N, 124° 17'W.
5. S.O.B.C.-Shell Beavercrow #1; 60° 02'N., 125° 01'W.
6. Gulf States Fort Nelson #2; 95-J-94-J-10: 58° 45'N, 122° 42'W.
7. Gulf States Evie Lake #1; 89-G-94-J-14: 58° 54'N, 123° 15'W.
8. Pacific-S.R.-Del Rio Kledo #1; c-14-G-94-J-13: 58° 51'N, 123° 41'W.
9. Toad River Joint Venture #1; 98-D-94-N-7: 59° 21'N, 124° 59'W.
10. Surface section 25 BR 64: 57° 56'N, 123° 43'W.
11. Surface section P3-63: 58° 35'N, 124° 34'W.
12. Surface section P1-63: 58° 50'N, 124° 57'W.
13. Shell East Grayling: d-95-F-94-N-11: 59° 37'N, 125° 19'W.

For the subsurface control points the drilling samples were examined and described under the binocular microscope. About thirty chips were selected as representative of each ten foot interval, with guidance from electric, sonic and radioactivity logs. All lithologies other than shale were later removed and the remaining chips grouped into composite samples covering 100 foot intervals. These composite samples, representing only shales, contained from two to four grams of material. In the compositing of samples care was taken to avoid including obvious lithologic breaks within any one composite sample.



INDEX MAP

FIGURE 1

Two surface exposures totalling 3800 feet were measured, described and sampled by the author, using a five foot sampling interval. In addition, samples from the Besa River type section were kindly provided by Dr. E. W. Bamber. All surface samples were broken open and small chips selected from the unweathered interior. These were then also composited into 50 or 100 foot intervals, as for the subsurface samples. It is felt that the surface sampling procedure is more biased than the subsurface procedure due to subjectivity as to representativeness, selectivity imposed by varying weathering characteristics, and the necessity of employing interval sampling as opposed to the "channel sampling" which is achieved by the drilling bit.

The above procedures involved description and sampling of 67,000 feet of section, of which some 45,000 feet consists of shale or very shaly intervals. Because of time limitations, the mineralogical and geochemical analysis of thick and megascopically homogenous intervals was limited to alternate composite samples. Thus the analyses presented herein represent approximately 31,000 feet of shale, or about 67% of the amount present at the chosen control points.

The lithologic description and examination of well logs in themselves provide some basis for correlation. It will be of interest, therefore to examine Figures 2, 3 and 4, which show what are felt to be conservative correlations based on the above criteria. These figures also demonstrate that the Besa River equivalents of the Fort Nelson area can be divided into a considerable number of formations. These formations provide a basis for the positioning of time divisions, at least approximately, to the stage level on the basis of previous work in this and adjacent areas, as indicated in Table I.

#5

#4

#3

#2

#1

FANTASQUE

MATTSON

BESA RIVER FORMATION

"LOWER ELK POINT GROUP"

DEBOLT

SHUNDA-PEKISKO

BANFF

Exshow

Kotcho

Tetcho-Trout River Kakisa

Redknife

FORT SIMPSON

Muskwa

HORN RIVER

KEG RIVER

Slave Pt.-Presqu'ile

Chert

Limestone

Inb'd Ls. & Sh

Dolomite

Shale

Siltstn; intb'd Ss. & Sh

Sandstone; Quartzite

0 5 10

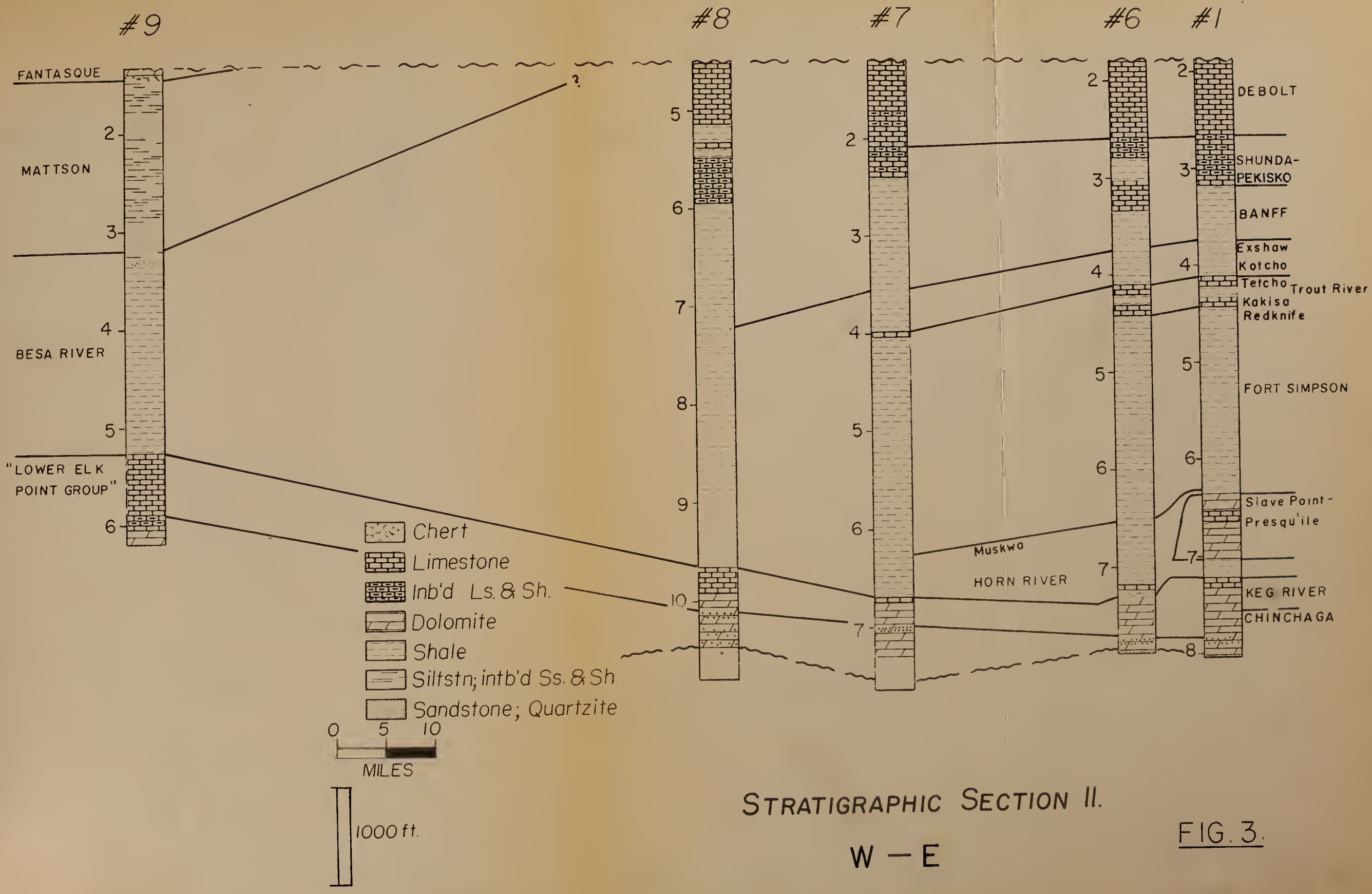
MILES

1000ft.

FIG 2.

STRATIGRAPHIC SECTION I.

NW – SE



STRATIGRAPHIC SECTION II.

W — E

FIG. 3.

#10 #11 #12 #9 #13 #5

PROPHET FM.

BESA RIVER FM.

FANTASQUE FM.

MATTSON FM.

Chert
Limestone
Intb'd Ls. & Sh.
Dolomite
Shale
Siltstn; intb'd Ss. & Sh.
Sandstone; Quartzite

0 5 10
MILES

1000 ft.

STRATIGRAPHIC SECTION III.
S — N

FIG. 4.

CHAPTER TWO

MINERALOGY

A. Techniques

Because of their extremely fine grain size and mineralogical complexity, shales are not amenable to megascopic or even to microscopic description. The best tool available for the investigation of shale mineralogy is the X-ray diffractometer, which provides a rapid qualitative evaluation and, under controlled conditions, a semi-quantitative evaluation of the mineral content. Over the past few years a number of shale studies utilizing the X-ray diffraction method have been reported (cf. Glass, 1956; Burst, 1957; Weaver, 1958; Speights and Brunton, 1961).

With few exceptions, previous studies have been limited to the mineralogy of the clay fraction. The technique most generally employed has been a rather time consuming one, involving disaggregation of the shale, separation of the clay fraction by settling in water, and sedimentation of the clays onto a glass slide or porcelain plate so as to achieve a high degree of preferred orientation. Experiments with this technique in the present study proved unsatisfactory because of the high organic content of the shales. It was found that the organic matter dispersed in the water, preventing effective gravity separation and inhibiting preferred orientation in the sedimented material.

Since the technique to be adopted for X-ray fluorescence analysis involved pressing the powdered shale into a briquet with cellulose backing at a pressure of 30,000 p.s.i., the utilization of these briquets for the diffraction study was evaluated. It was found that the briquets yielded a strong series of diffractions from the basal planes of the clay minerals, exhibiting intensities 1.5 times greater than sedimented slides and 2 to 3 times greater than loosely packed powders. In addition, it was found that the principal diffraction peaks of quartz and of the carbonate minerals showed considerably enhanced intensities, probably due to

increased density of the sample and to the smooth and glossy surface which the briquet presents to the incident beam.

In order to ensure that the briquetting pressure produced no changes in lattice structure of the various minerals, diffractograms of loosely packed powders were carefully compared with those of the briquets. In addition, comparative runs were made on an A.P.I. montmorillonite in both dry and glycolated state. In no case could any difference be noted between powder and briquet diffraction patterns, other than enhanced reflection intensities. Similar studies by Chillingar, Rieke and Robertson (1963) on dickite and halloysite at pressures up to 120,000 p.s.i. similarly show no change in the lattice structure of those minerals. It was concluded that the pressed briquet was a safe and effective medium for the mineralogical study.

It has already been indicated that disaggregation and homogenization of the composite sample was achieved by grinding. Grinding periods selected were 15 minutes in a power mortar initially and later, when it became available, one minute in a Bleuler rotary mill. The effect of grinding was evaluated by comparative diffractometer runs on the same sample with grinding times ranging from 1/3 to 2 times the standard grinding period. No differences were noted in either pattern or intensity of the diffraction peaks. Previous studies by MacKenzie and Milne (1953) and by Takahashi (1957) serve to confirm that no deleterious effect should be anticipated for grinding periods of the order used.

Equipment employed for the diffraction analyses was a Phillips Norelco Type 12045 B/3 unit, with a copper tube operated at 35 kilovolts and 15 milliamps. Instrument settings used were scale factor of 4, multiplier of 1 and time constant of 4. Each briquet was scanned over the two theta range 4° to 34° at a scanning rate of one degree per minute, and the diffractogram recorded on a Brown strip chart recorder. The scan interval includes the principal peaks of the clay minerals, quartz, feldspars and carbonates.

B. Quantitative Estimates

The diffraction intensity observed for a given set of planes of a given mineral in a mixture will depend on the scattering co-efficient of the planes, the average orientation of the grains, the absorption co-efficient of the matrix, the statistical accuracy of the counter and the amount of the mineral present. To achieve an estimate of the amount present, it is necessary to assume that the scattering co-efficient, average orientation and absorption co-efficient remain constant from sample to sample and between sample and standards.

So long as the chemical constitution of the mineral remains constant, the condition of constant scattering co-efficient will hold. This is the case for most minerals, but deviations are possible in the case of the clay minerals, which are capable of a high degree of ionic substitution. Constant and random orientation would be anticipated for quartz because of the absence of prominent cleavage, and constant and preferred orientation would be expected for the clay minerals because of their single perfect cleavage. For carbonate minerals one would expect to find a high degree of preference for orientation on one of the three equally developed cleavages but with random selection among the three, i.e. a high degree of uniformity of average orientation. The assumption of constancy of absorption co-efficient will probably be met within reasonable limits so long as we confine the analyses to one major rock type and assure a similar mineralogical and chemical composition for the standards.

The carbonate minerals had been found to occur in minor amounts, and it was possible to select shale intervals in which any one mineral was not present in detectable quantity. By the addition of known quantities of the unrepresented carbonate, it was possible to prepare sets of standards containing known amounts of each carbonate. Quartz, in contrast, appeared to be a major constituent in all samples, and consequently a set of standards was made up using illite, chlorite and

cellulose in the ratio 8:1.5:0.5 respectively as a matrix material to approximate the average shale composition.

The above procedures yielded standard sets for calcite, dolomite, siderite and quartz. Each set was pressed into briquets and repeated runs were made concurrently with the shale analyses at regular intervals to provide calibration curves for the conversion of measured intensities to percentages. Examples of these calibration curves are given in Appendix A.

Repeated runs on individual shale samples showed standard deviations in the range of $\pm$ 1% to $\pm$ 5%. Repeated runs on the standards however showed deviations in the range of $\pm$ 12% to $\pm$ 20%. This difference obviously reflects the difficulty of homogenizing the added mineral into the matrix without excessive grinding. This large potential source of error was minimized by averaging fifteen or more determinations for each point on the working curves. Overall accuracy of the quantitative estimate is difficult to evaluate, but it is felt that it lies somewhere between the 5% minimum precision of the analytical determinations and the 20% minimum precision of the standard determinations, and is probably closer to the former figure than the latter.

Quantitative evaluation of the clay minerals proved more difficult. A set of illite-chlorite mixtures was prepared and pressed into briquets. Because of the diffuse nature of the illite peak in particular, peak area as determined by planimeter was taken as a measure of intensity rather than peak height. Plots of peak area versus weight percent showed, as illustrated in Appendix A, a most unacceptable scatter of points. Since the divergence from a linear relationship varies in the same direction for both chlorite and illite in a given standard, it is reasonable to assume that the scatter is due to variability in the degree of preferred orientation from standard to standard.

Johns, Grim and Bradley (1954) have suggested an approach which obviates this difficulty and their method, with modifications, has been followed by Schultz

(1955), Freas (1962) and others. Briefly, the method consists of establishing the comparative scattering co-efficients of the basal planes of the various clay minerals and using these to normalize observed intensities, thereby permitting calculation of the proportions of the various minerals present in the mixture. The plot of peak area versus weight percent indicates that the average intensity of the chlorite 002 peak is almost exactly four times that of the illite 001 peak. Thus it is evident that the proportion of a given mineral in the clay fraction can be calculated from the normalized peak area ratios, for example:

$$\% \text{ Illite (in clay fraction)} = \frac{\text{Illite 001 area}}{\text{Illite 001 area} + (\text{Chlorite 002 area} \div 4)} \times 100$$

This method will be independent of orientation as long as each of the clay minerals in a given sample is oriented to the same degree. Brindley (1961a) has stressed the importance of ensuring that any external clay mineral standards closely approximate the characteristics of the minerals in the sample to be analysed. It should be noted therefore that the 1:4 ratio quoted here for Illite 001:Chlorite 002 applies to the A.P.I. Fithian illite and to a chlorite with 001:002 intensity ratio of 1:2. Both of these minerals closely approximate the average characteristics of those observed in the Besa River shale.

Having determined the proportions of the clay minerals, it was now necessary to determine the clay fraction in each sample. This was done by difference, employing quartz and carbonate mineral percentages determined by the diffraction method and pyrite as calculated from the sulphur analyses of the fluorescence study. An allowance of 5 percent was made for interstitial water plus organic matter and the remaining balance was assumed to be clay minerals.

Application of the normalized peak intensity ratios to the prepared standards yielded proportion estimates which were well within 5 percent of the correct values, as illustrated in Appendix A. It is obvious however, that the accuracy of the

percentage estimate for each clay mineral in the total rock can be no greater than that with which the other mineral components were determined. In general it will in fact be less, because of variations in scattering power due to variations in chemical composition of the clay minerals.

Pyrite and feldspar were two other minerals regularly observed in the diffraction pattern. Peak heights were small, and no attempt was made to quantify these minerals by the diffraction method. The pyrite content is felt to be adequately represented by the sulphur analyses of the fluorescence study, and feldspar is a trace constituent which, on the basis of limited petrographic examination, seldom if ever exceeds two percent.

C. Discussion of Mineral Species

Quartz

Because the principal peak 101 of quartz is coincident with the moderately strong 024-006 diffraction from illite, it was necessary to employ the quartz 100 peak for quantitative estimates. All quartz peaks were sharp and well defined and were used as an internal standard for the accurate measurement of the d-spacings of other minerals.

Petrographic evidence had suggested that much if not all of the quartz has originated as opaline or amorphous silica, raising the question of whether amorphous silica might still be represented in the shales to some degree. Since the amorphous form would not contribute to the diffraction pattern a comparison of SiO_2 as determined by fluorescence analysis with the SiO_2 as calculated from the diffraction mode should provide a check on this possibility. Because of the difference in accuracy of the two methods, this comparison was averaged over fifteen samples in each of two wells. The SiO_2 as calculated from the diffraction mode was found to average 1 percent lower than the fluorescence analyses in one instance and 2 percent lower in the second. This difference is scarcely large enough to permit an assertion

that some amorphous silica is present, but certainly the close agreement does permit the conclusion that if it is present it is in very small amounts.

Calcite

The principal peak 104 of calcite, which was used for the quantitative estimates, was found to deviate very little from a d-spacing of 3.03Å. According to Graf and Goldsmith (1958), this spacing is indicative of a very minimal amount of $MgCO_3$ in the crystal lattice, in the order of one to two mole percent. Low magnesium calcite is characteristic of inorganic deposition (cf. Revelle and Fairbridge, 1957) as contrasted with the high magnesium calcites of organic origin. This criterion applies only at the time of deposition however, since the high magnesium form is unstable and tends to unmix to calcite and dolomite. In the present study the calcitic shales almost without exception also contain some dolomite. This fact, plus petrographic evidence to be cited later, suggests that most of the calcite present is of organic origin.

The ubiquitous occurrence of pelagic calcite-secreting organisms in modern oceans is evidenced by the widespread development of deep sea calcitic oozes. The ubiquitous presence of calcite in the shales of the more easterly control points suggests a similar situation during Devonian and Mississippian sedimentation. The disappearance of calcite in the more westerly control points can therefore logically be attributed to bottom or immediately sub-bottom conditions in which the pH was below 7.8, the "limestone fence" of Krumbein and Garrels (1952). Physical evidence of calcite solution in the form of ostracod molds was observed.

It should be mentioned that the high mobility of calcite gave rise to a problem in the form of secondary veining within the shales. All chips showing evidence of such veining were discarded during the binocular microscopic examination, but the possibility of contamination by sub-microscopic veinlets cannot be disregarded.

Dolomite

The principal peak 104 was used for quantitative estimates. This peak varied only slightly from a d-spacing of 2.90Å, which is slightly higher than the "normal" 2.88Å spacing and indicates the presence of some calcium carbonate in solid solution. Sabins (1962) has interpreted this type of dolomite, on the basis of petrographic examination, as being of secondary origin, and ascribes to the 2.88Å variety a primary or detrital origin.

In view of what has been previously stated concerning the unmixing of magnesian calcite, we might assume that the 2.90Å dolomite of this study is "unmixed" secondary dolomite, in support of Sabins' view. However, several intervals are found in which dolomite is present without any calcite; this dolomite is clearly not the product of such an unmixing process. It could be interpreted as primary dolomite, similar to that which Fairbridge (1957) reports forming in recent deep water sediments. Such an interpretation would, however, conflict with Sabin's observations.

Siderite

Siderite has been identified and the amount estimated on the basis of the principal peak 104 at a d-spacing of 2.80Å.

Although the amount of siderite present never exceeds four percent, the occurrence of the mineral as the principal carbonate species in some intervals is considered significant. "Ironstone" concretionary material was frequently observed in the microscopic examination, and was all discarded as indicative of a micro-environmental condition. The siderite appearing in the analyses is therefore not concretionary but disseminated, and may be assumed to be an indicator of the major environment.

Garrels (1960) has demonstrated that the formation of siderite requires a virtual absence of oxygen. Utilizing his diagram of the stability field of siderite

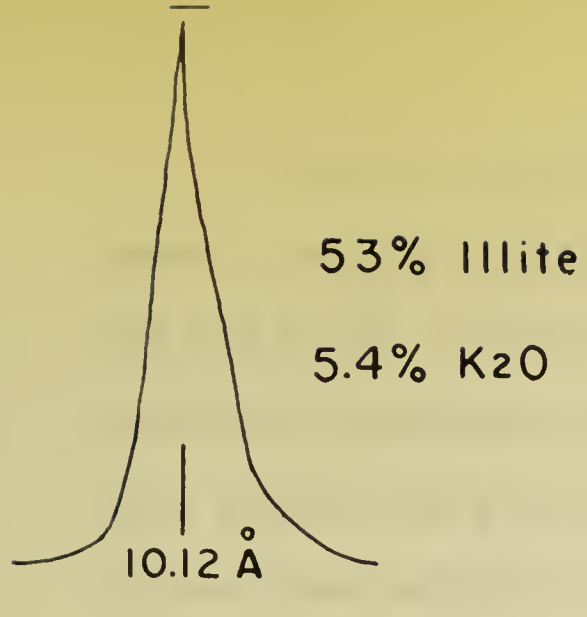
and giving consideration to the position of the "limestone fence", it would appear that precipitation of siderite without calcite, as observed in most of the siderite intervals of this study, would indicate a pH in the range of 6 to 7.8 and an Eh of between 0 and -0.4.

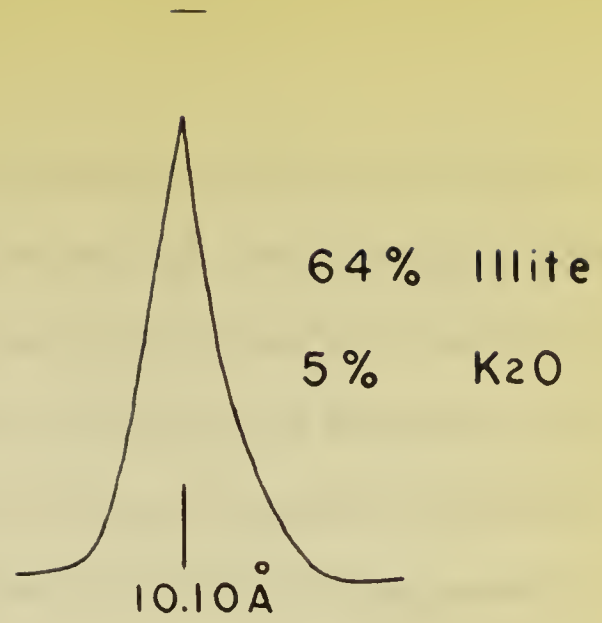
It seems reasonable to assume that the partitioning of the three carbonate species is closely controlled by the bottom or immediate sub-bottom environment. The presence of calcite would indicate a pH of above 7.8, while the presence of siderite without calcite would suggest a pH between 6 and 7.8. The presence of dolomite alone may indicate some intermediate and as yet undetermined pH range. The absence of all three carbonates in some of the more westerly control points might suggest the possibility of a pH value lower than 6, although ZoBell (1946) indicates a lower pH limit for recent marine sediments of 6.4

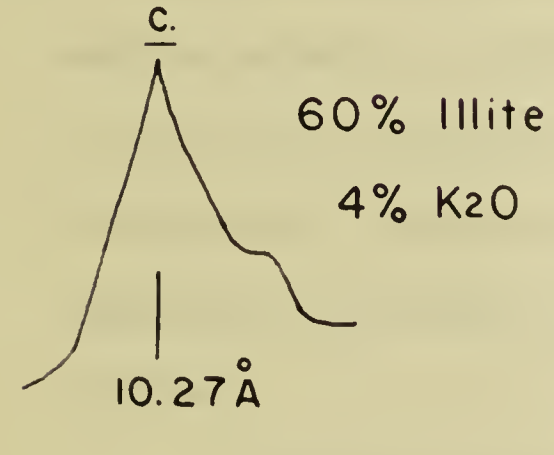
Illite

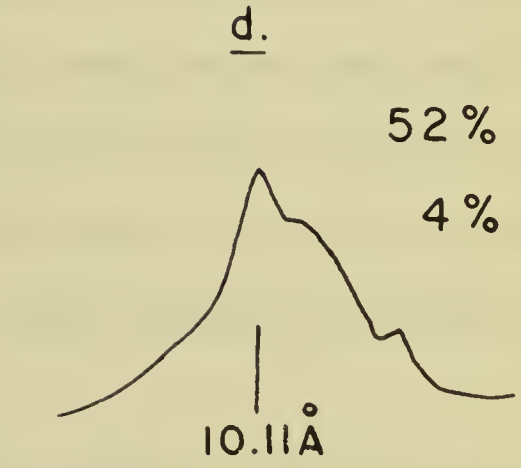
The mineral herein reported as illite encompasses the broadest definition of that term, i.e. "those of the clay mineral constituents of argillaceous sediments belonging to the mica group" (Bradley and Grim, 1961). Sufficient variation exists from sample to sample to suggest sericite, muscovite, illite, "degraded" illite, hydromuscovite, glauconite and mixed layer illite-montmorillonite. This range of variation insofar as it affects the principal peak is illustrated in Figure 5, together with the estimated percentage of the mineral in the sample and the K_2O analysis of the sample as recalculated to the illite fraction alone.

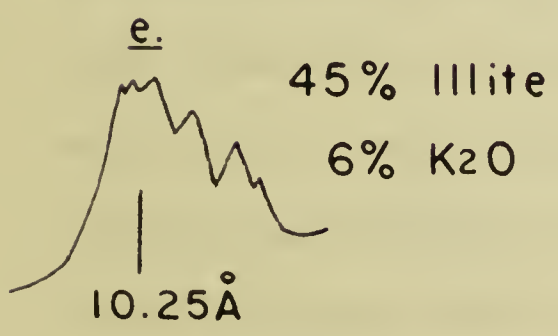
From Figure 5 it is evident why it is necessary to employ peak area rather than peak height for quantitative estimation (cf. a versus d). It also appears probable that the potassium content of the mica has a considerable effect on peak broadening (cf. a, b, c). That this is not the sole factor affecting peak shape is indicated by a comparison of curves a and e or c and f. In such cases the dominating influence may well be the degree of hydration of the interlayer position.

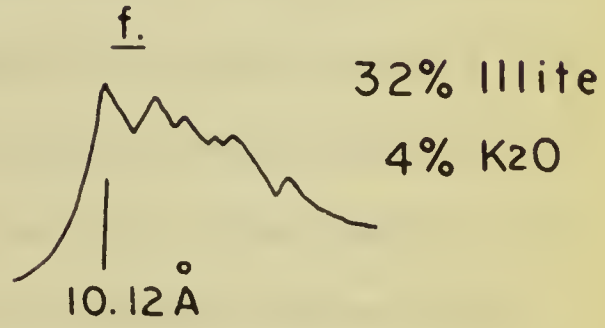












VARIATIONS IN ILLITE PEAK SHAPE

FIGURE 5

It will be noted that the d-spacing indicated by the highest peak of the pattern is usually a small but significant amount on the high side of the usual illite peak at 9.9-10Å. That this is probably indicative of a small degree of random interstratification with montmorillonite is indicated by a slight shift in the peak towards higher spacings upon glycolation. Application of the visual inspection method of MacEwan, Amil and Brown (1961) suggests that the montmorillonite component is seldom greater than 20 percent and is generally much less than this.

Fawcett (1964) has demonstrated the transformation of mixed layer illites to illite plus chlorite plus quartz at a temperature of about 300°C. This reaction would undoubtedly proceed at a slower rate at lower temperatures, and it is possible to visualize the variations in "illite" observed in this study as various stages in this transformation. That mixed layer illite is the "parent" clay mineral might also be suggested by the fact that it is the only one which occurs to the exclusion of other varieties.

The close interdependence of montmorillonite, illite and chlorite on the nature of the physiocochemical environment has been indicated by several workers. Henin (1955) has demonstrated the precipitation of montmorillonite from dilute solutions at pH values of 7 to 11; below pH = 7, oxides or hydroxides were obtained. In the presence of potassium, illites were also precipitated. Earlier, Caillere and Henin (1948, 1949) had demonstrated the transformation of montmorillonite to illite and to chlorite. Whitehouse and McCarter (1958) have also demonstrated the conversion of montmorillonite to illite and chlorite in sea water under laboratory conditions, and Powers (1957) has suggested conversion of illite to chlorite during diagenesis as well as the reverse reaction after burial.

On the assumption that what has been observed in the laboratory under conditions prevailing in nature is very apt to constitute a feasible natural process, it is accepted as a working hypothesis that clay minerals are capable of being formed as direct precipitates from sea water under some conditions, and furthermore that they

are subject to early diagenetic alteration in response to the physiochemical environment, at least to the degree of the montmorillonite-illite-chlorite transformations which have been observed.

Chlorite

Association of the 7Å peak of this study with chlorite and septechlorite requires some explanation, and perhaps some reservation. In the majority of the samples, a diffraction peak at 7.11 to 7.20Å was accompanied by a weak peak at 14.10 to 14.50Å. Slow scans of the 7Å peak and subsequent orders gave no reason to suspect kaolinite and therefore in the majority of samples the peak is due to an iron-rich normal chlorite with, in general, a rather low degree of aluminum substitution in the tetrahedral layer.

In other samples however, and in many instances from units stratigraphically equivalent to those containing the normal chlorite, the 14Å peak is absent, but a peak at 7.11 to 7.21Å is still observed. Again slow scanning of subsequent orders suggests, in most samples, that only one mineral species is present. The question arises whether this mineral is a septechlorite or a kaolinite.

Warshaw and Roy (1961) have discussed the difficulty of distinguishing these two mineral species, and have recommended treatment with hot 2N acid to attack the septechlorite. This procedure was applied to two samples, together with a normal chlorite and kaolinite as controls. After a digestion period of 2 1/2 hours at 80°C, the following results were noted.

	Intensity of 7Å peak	
	Before	After
Shale sample #1	43	35
Shale sample #2	62	50
Kaolinite	54	55
Normal chlorite	72	97

These results, which in the absence of controls could have been interpreted as positive

evidence of at least some chlorite in the shales, underline the cautions which Brindley (1961b) has urged regarding the dependence of acid reaction on particle size and chemical composition. The enhancement of the normal chlorite can only be attributed to "cleaning up" of the sample (e.g. removal of iron oxide) and possibly to some recrystallization.

Heat treatment has also been suggested frequently as a means of differentiation between chlorites and kaolinites. One sample was therefore subjected to temperatures of 475° and 575°, again with kaolinite and normal chlorite as controls, for one hour:

	Intensity of 7Å peak			
	Before	475°	Decrease	575°
Shale sample #3	33	13	60%	0
Kaolinite	53	14	74%	0
Normal chlorite	71	38	47%	24

It is apparent that the direction of behaviour of all three samples is similar, and the rate of reaction of the unknown is almost exactly intermediate between the two controls. Again, considering uncertainties introduced by grain size and chemical composition, the result is indeterminate.

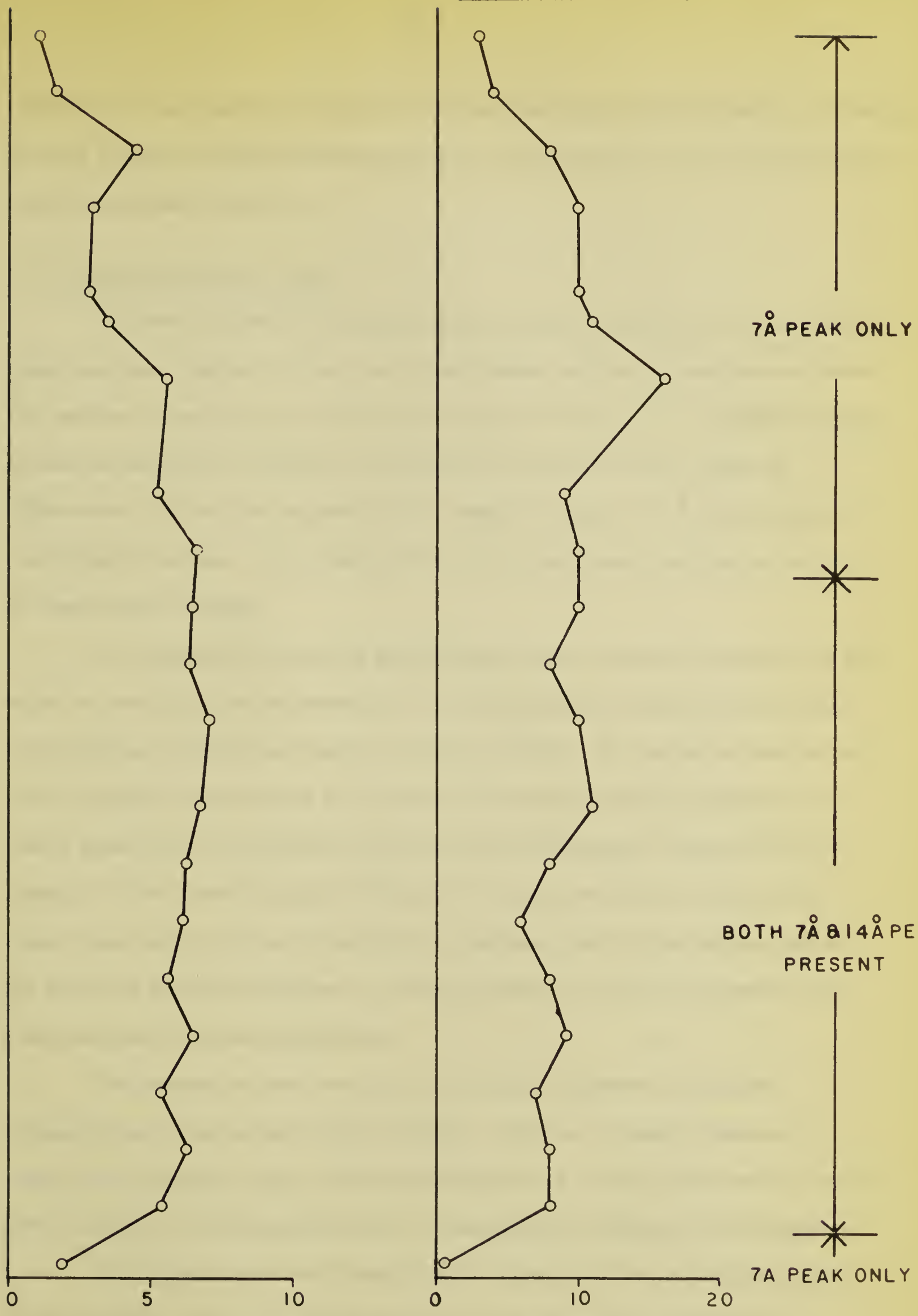
Biscaye (1964) has argued that the generally somewhat smaller basal spacings of the common septechlorites should permit differentiation from kaolinite. As previously indicated, the slow scan applied to this problem shows 7Å spacings in the kaolinite range. In addition, a 2.38Å diffraction peak is observed, which Biscaye regards as confirmation of kaolinite. The evidence is weakened however by the presence of a 2.38Å peak in the control normal chlorite. Moreover, Biscaye's argument relative to the lower basal spacings of the septechlorites seems to ignore the evidence of Nelson and Roy (1958) that septechlorite spacings, like those of the normal chlorites, vary in response to the degree of aluminum substitution in the octahedral layers. The range of variation completely overlaps the spacing of kaolinite.

One other criterion mentioned by Brindley (ibid) and by Warshaw and Roy (ibid) is the 060 spacing, which is 1.48 Å for the dioctahedral kaolinites and 1.54 Å for the trioctahedral chlorites. Examination of 060 intervals on a number of samples powders yielded 1.54 Å peaks in all cases, but little evidence of coherent energy at the 1.48 Å spacing. The results here are suspect because of coincidence of the 1.54 Å peak with the 211 spacing of quartz and because of a very weak 060 peak from the undiluted pure kaolinite used as a control.

Differential thermal analysis in a nitrogen atmosphere was also performed on one shale sample and on control minerals. To be brief, no objectively conclusive result could be determined.

In the absence of a conclusive mineralogical determination, the evidence of the major oxide analyses was considered. Since the 7 Å mineral is almost exclusively confined to siderite bearing units, indicative of a rather strongly reducing environment, the presence of glauconite does not seem too great a probability. Thus the iron content of the shales will reside in pyrite, siderite and chlorite. Since the pyrite content is known through the sulphur analyses and the siderite content by diffraction analyses, it is possible to compute the "residual iron" for each sample. The "residual iron", if present in any substantial amount, should indicate the presence of chlorite, and in the absence of any other 7 Å mineral, should show a direct correlation to the intensity of the 7 Å peak.

Figure 6 shows a plot of the "residual iron" for a section of one well,across the zone of transition from a 14 Å to a 7 Å mineral, together with a plot of percent chlorite as calculated from 7 Å peak intensity. It can be seen that the "residual iron" is high enough to suggest the presence of chlorite throughout and, in general, the correlation of 7 Å peak intensity to "residual iron" is close enough to suggest that chlorite is the principal contributor to that peak. The average "residual iron" content of the entire interval is 3.35% and the average estimated chlorite content is 7.93%, indicating a mineral of about 42% Fe content. This plus the low octahedral aluminum indicated by the basal spacing suggests a mineral closely approximating



Comparison Of "Residual Fe2O3" To 7Å Peak Intensity

FIGURE 6

clinochlore in composition. It is thus concluded that the principal minerals contributing to the 7 Å peak are chlorite and septechlorite. The presence of very minor amounts of kaolinite remains a possibility.

D. Correlation by Mineral Logs

In order to permit utilization of mineralogical variations as a correlation tool, these have been plotted as a function of stratigraphic position for each control point. The resultant mineral logs are illustrated in Figures 7 through 18. In addition to the mineral percentages as estimated from diffraction peak intensities, these logs differentiate chlorite from septechlorite by means of a plot of 14 Å peak intensity in the "chlorite" column. The chlorite/illite ratio has also been computed as an index of clay mineral variation.

The dashed line across the base of each column indicates the position of the top of the pre-Givetian carbonate unit, i.e. the approximate top of the Lower Elk Point Subgroup of Grayston, Sherwin and Allan (1965). The contention that the top of this carbonate approximates a time marker is strengthened by the presence of a clastic zone within the carbonate which can be correlated over wide areas, as for example in Stratigraphic Section II (Figure 3). In the immediate vicinity of Fort Nelson some buildup of the carbonate unit is evident, marking the introduction of the Keg River biostromal platform on which the Presqu'ile-Slave Point barrier complex subsequently became established.

The dashed line near the top of each mineral log marks the upward disappearance of predominant shale lithology. This line is strongly diachronic, marking the transition to Upper Mississippian carbonate at some points and the contact with the Mattson at those points where the Mississippian carbonate is not present.

Also indicated on the mineral logs, by letters, are the correlation points which have been used. It must be emphasized that because of the fairly large interval covered by the composite samples and because of gaps between samples, the

correlations can only be regarded as approximate. These same factors will also result in differences in the shape of the curves from point to point. It should also be appreciated that because of the very large area covered it would be unreasonable to expect any unit to maintain identical mineralogical character throughout and we must therefore proceed from control point to control point along each section, noting changes in character as they occur. Figures 7 through 18 are therefore arranged in sequential order corresponding to the arrangement of the three stratigraphic cross sections.

It would be an exhaustive procedure to discuss all of the correlations which have been made. The critical reader will wish to satisfy himself on the validity of the correlations, and we will therefore set forth in some detail the basis for the correlation of control points #1 to #5:

Control Point #1 (Clarke Lake c-94-L)-Figure 7.

P - Marks a gradational downward increase in carbonate content across the Pekisko/Banff contact.

E - Exshaw shale; marked by high quartz with all other minerals low and chlorite/illite ratio a minimum. The chlorite present is the 7 Å variety.

K - Calcite maximum within the Kakisa shale.

R - Quartz maximum, with illite minimum, local chlorite maximum and onset of downward decrease in calcite. Lies immediately below the Kakisa formation, therefore is the lateral equivalent of the Redknife shale.

M - Muskwa shale; high quartz, low clays, low carbonate, low chlorite/illite ratio and septechlorite rather than normal chlorite.

Control Point #2 (Snake River #A-1)-Figure 8.

S - Approximate Debolt/Shunda contact; marked by downward decrease in carbonates and illite, accompanied by downward increase in chlorite.

P - As in Figure 7.

E - As in Figure 7.

K - As in Figure 7.

R - As in Figure 7, but with chlorite maximum no longer evident.

M - As in Figure 7.

Control Point #3 (Deer Lake #A-1)-Figure 9.

S - Carbonates decrease as in Figure 8; quartz develops a minimum and illite a maximum.

P - As in Figure 8, but note development of high quartz content in interval above P.

E - As in Figure 8; note thickening of Exshaw Shale.

K - As in Figure 8.

R - Much as before; note return of local chlorite maximum.

X - Local low quartz, high clay unit.

M - As in Figure 8, except low chlorite/illite ratio no longer evident.

Control Point #4 (Beaver River #A-1)-Figure 10.

S - Positioning at downward disappearance of calcite confirmed by low quartz and high illite as seen at previous control point. Note development of a siderite-bearing unit below marker.

P - In the absence of calcite this correlation is now carried at the base of the high quartz unit which became well defined in Figure 9.

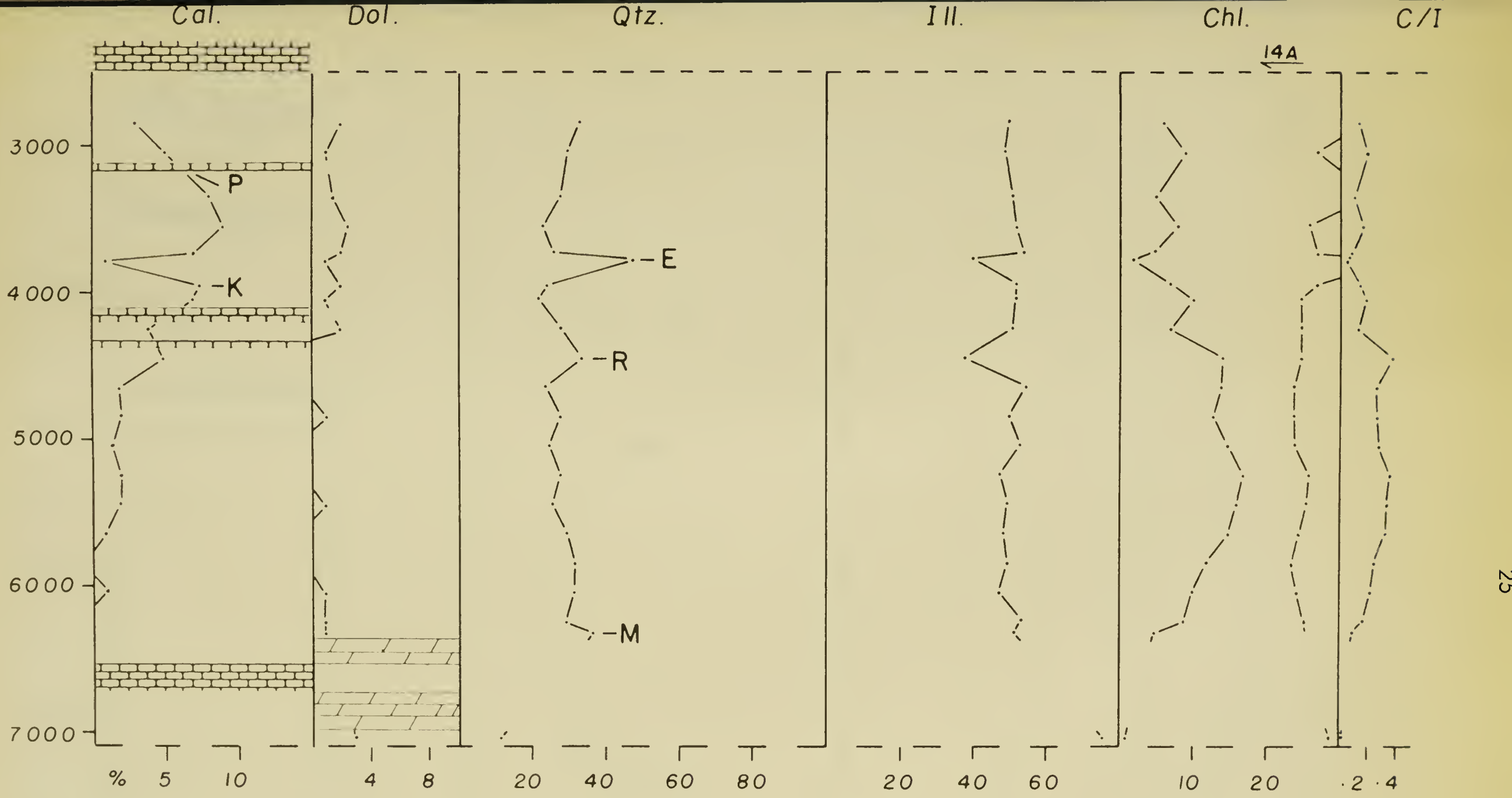
E - Carbonate content now a local maximum, otherwise as before. Overlying siliceous limestone unit may be upper part of the thick Exshaw Shale at control point #3, Figure 9.

K? - Dubious correlation, based on dolomite maximum and presence of a siliceous limestone.

R - As before, except for chlorite maximum.

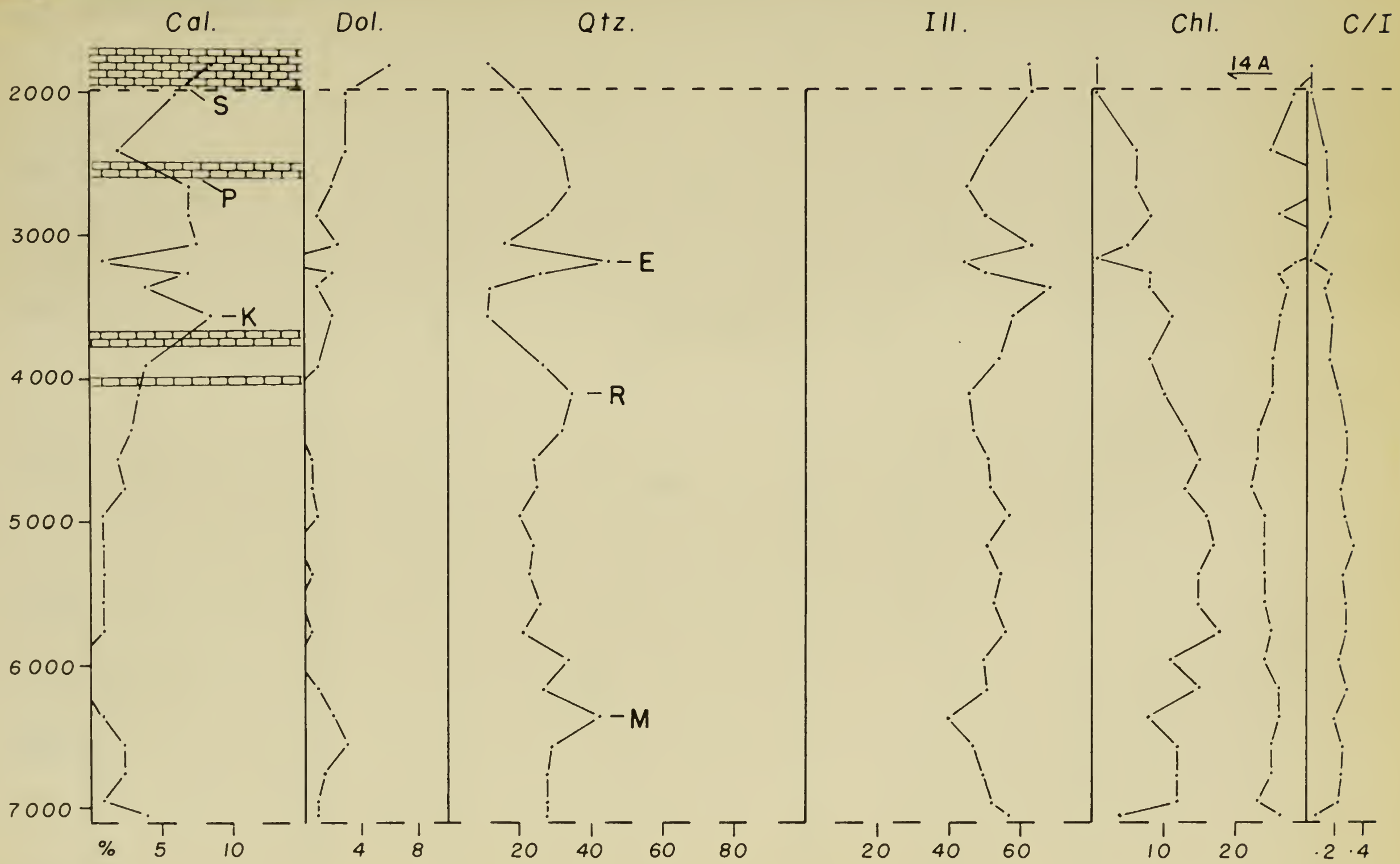
X - Local low quartz, high clay unit.

M? - Dubious; based on high quartz and low clays only.



1- Clarke Lake C-94-L: Mineralogy

FIGURE 7



2- Snake River A-1: Mineralogy

FIGURE 8

3000
4000
5000
6000
7000
8000
9000

S
P
K
P
E
R
X
M

% 5 10 4 8 20 40 60 80 20 40 60 10 20 ·2 ·4

3 - Deer Lake A-1 : Mineralogy

FIGURE 9

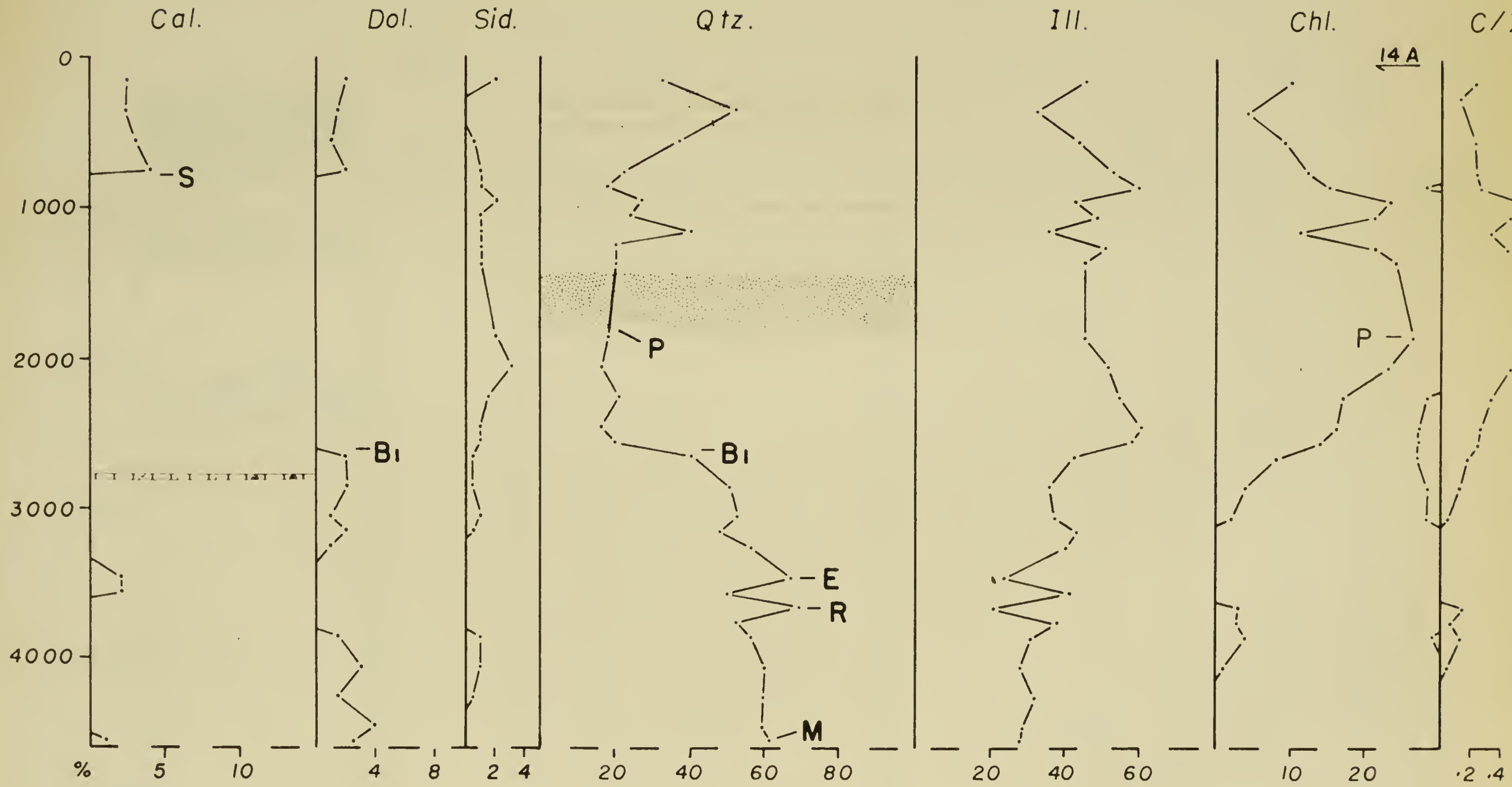
5000
6000
7000
8000
9000
10,000
11,000

S
P
K
E
R
X
M

% 5 10 4 8 2 4 20 40 60 80 20 40 60 10 20 .2 .4

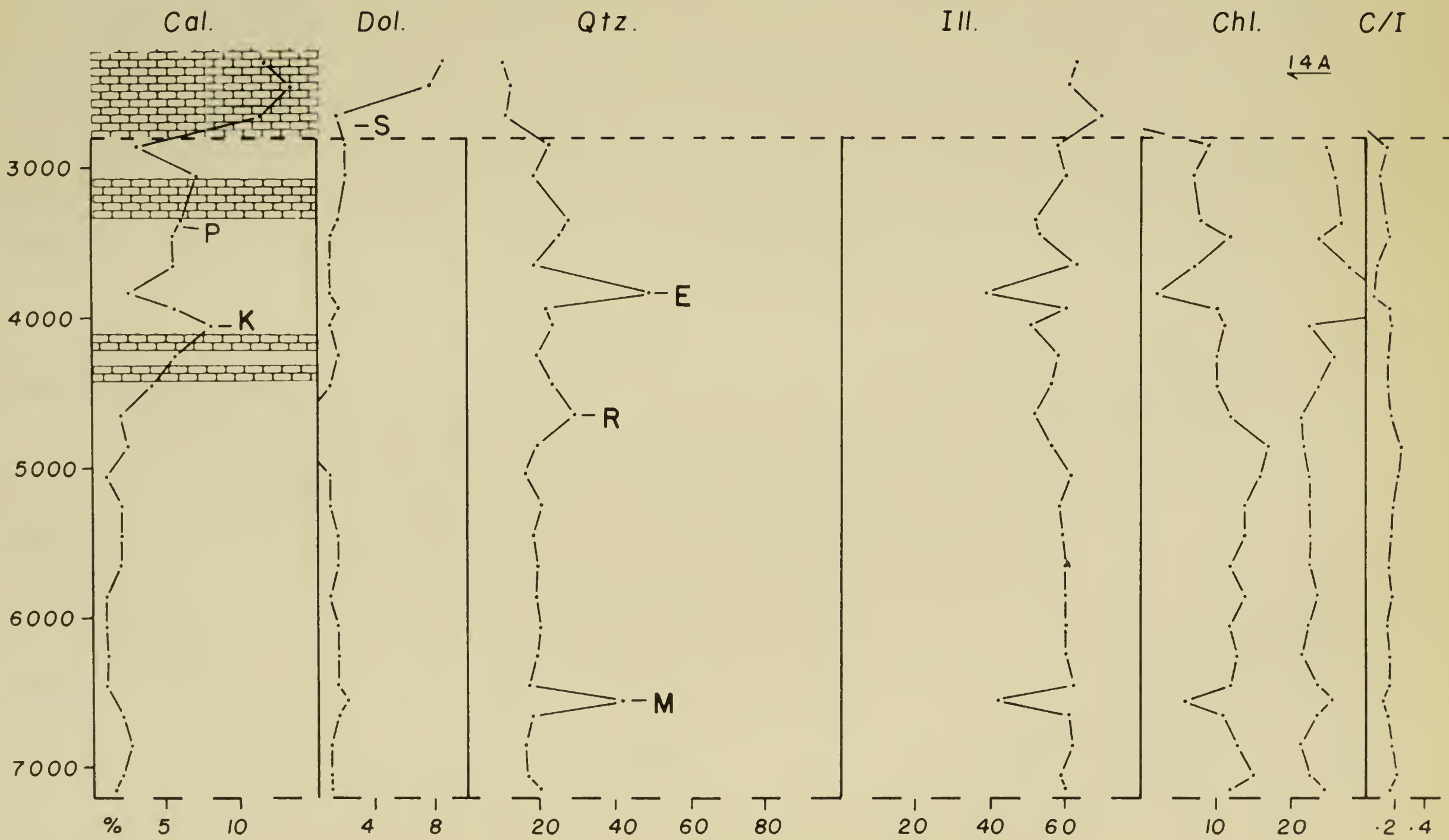
4- Beaver River A-1 : Mineralogy

FIGURE 10



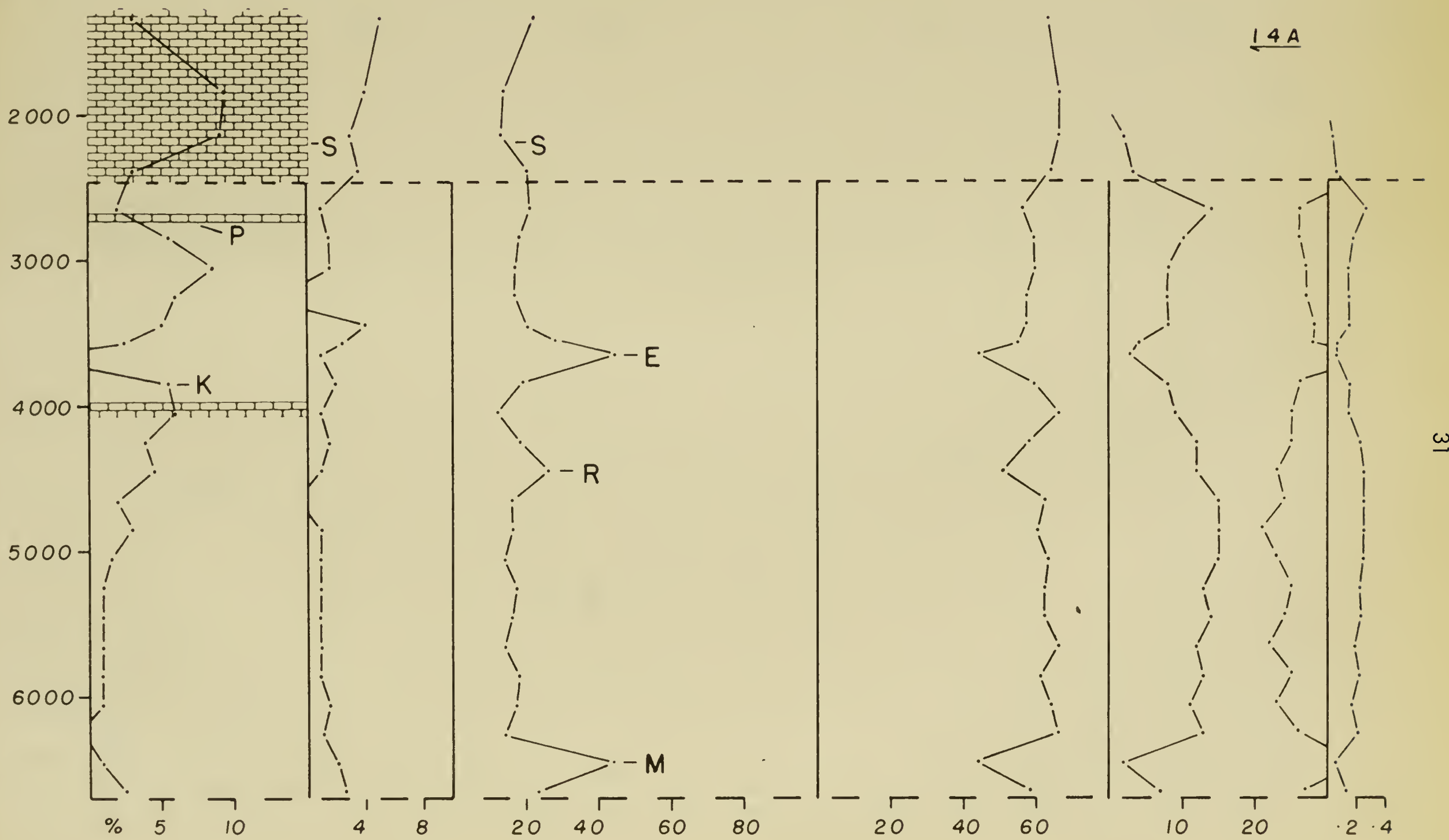
5 - *Beavercrow: Mineralogy*

FIGURE 11



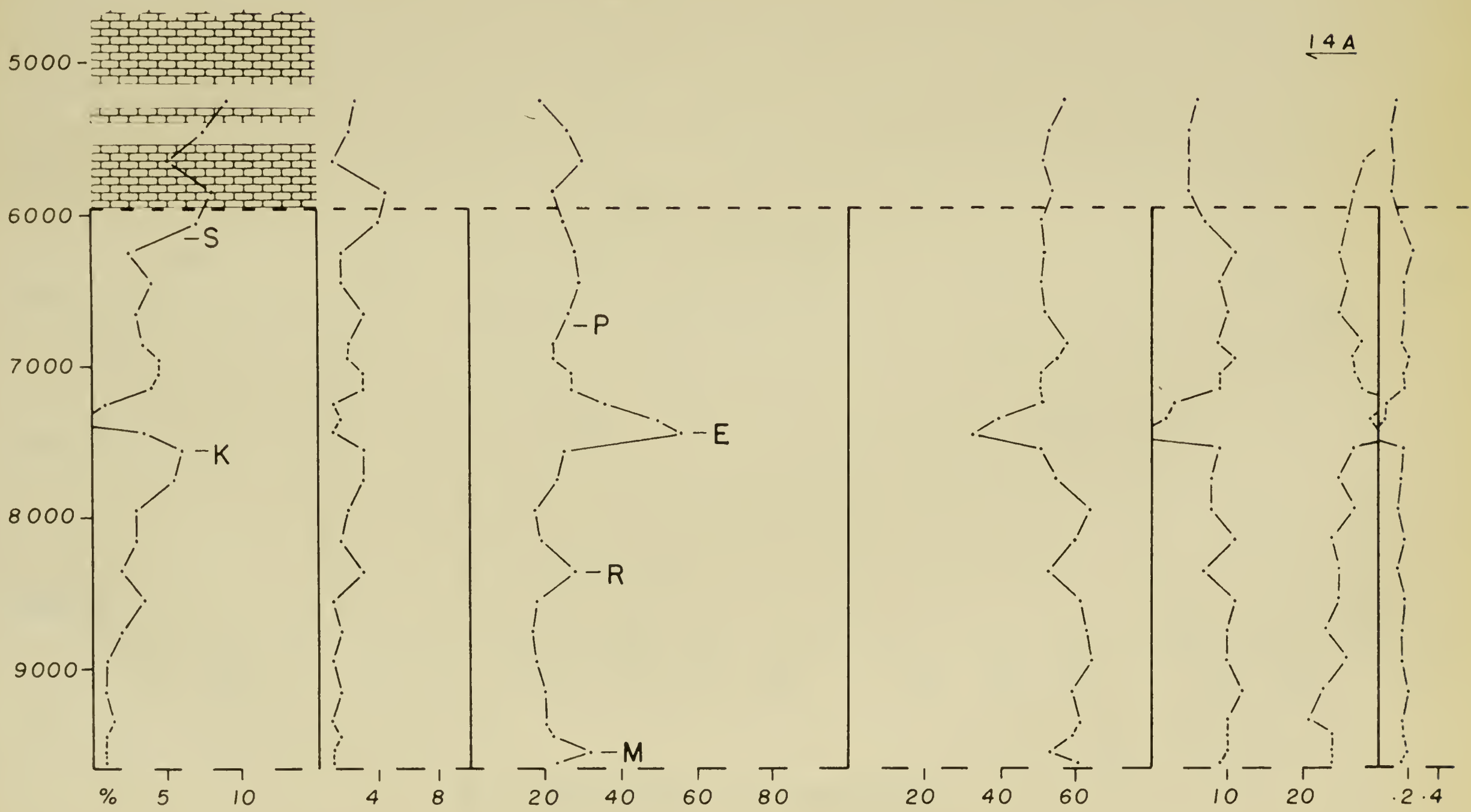
6 - Ft. Nelson #2 : Mineralogy

FIGURE 12



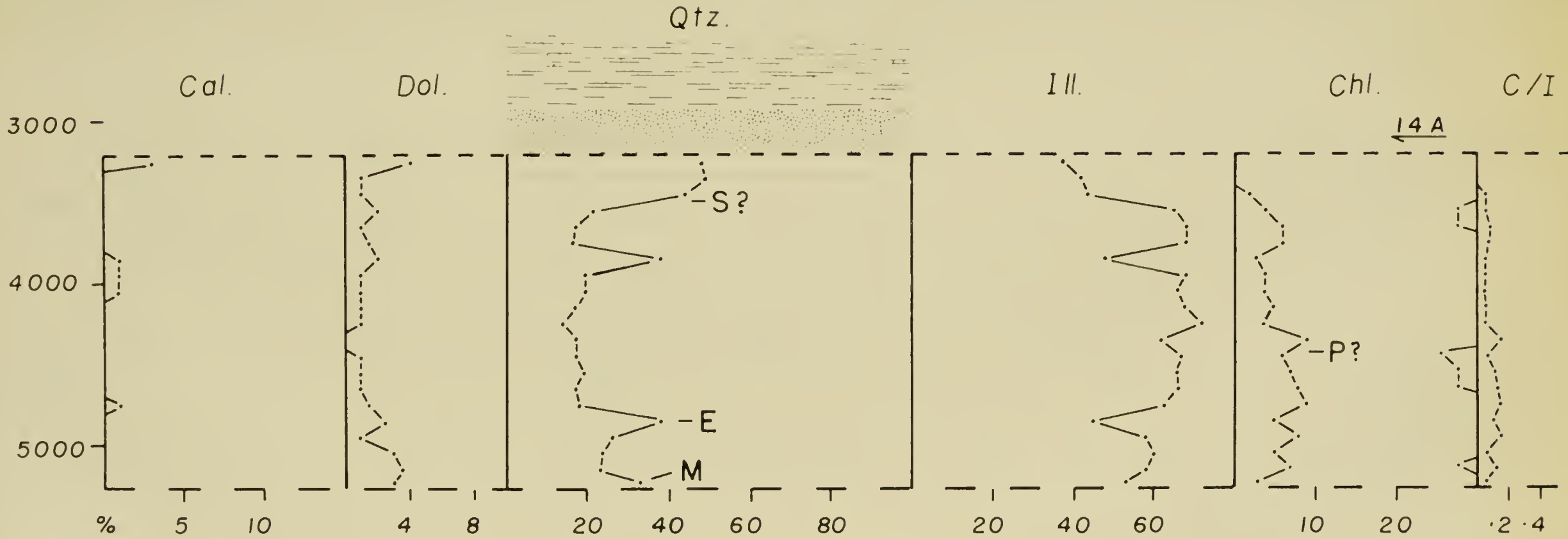
7 - Evie Lake #1 : Mineralogy

FIGURE 13



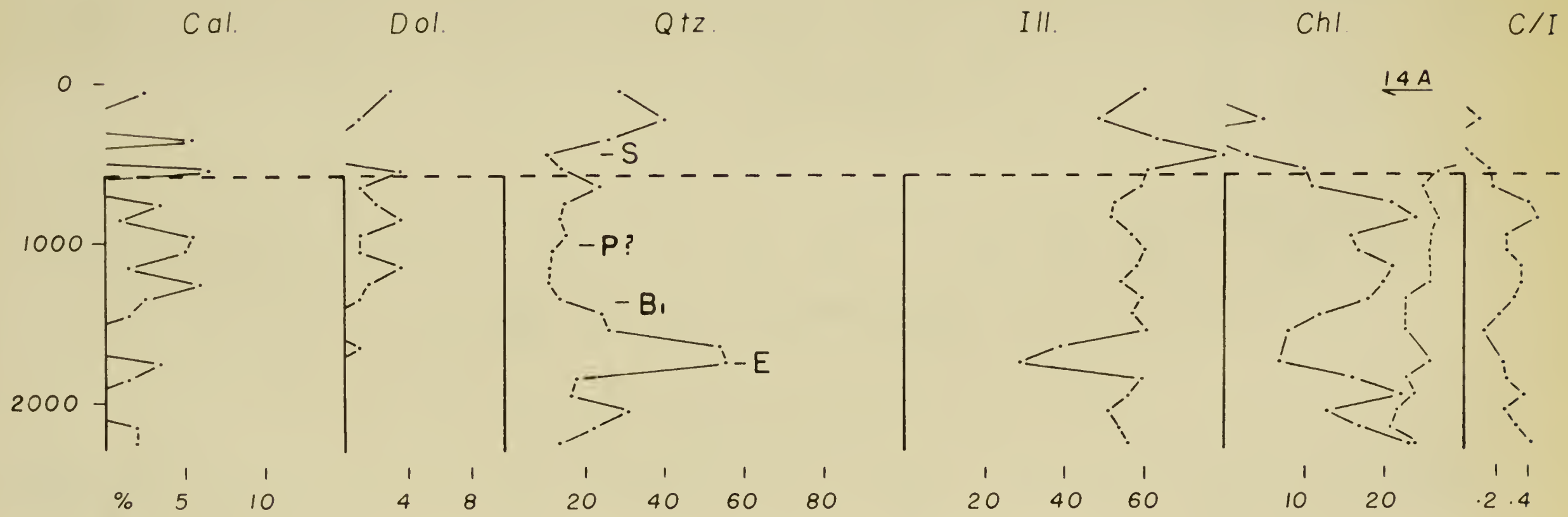
8 - Kledo : Mineralogy

FIGURE 14



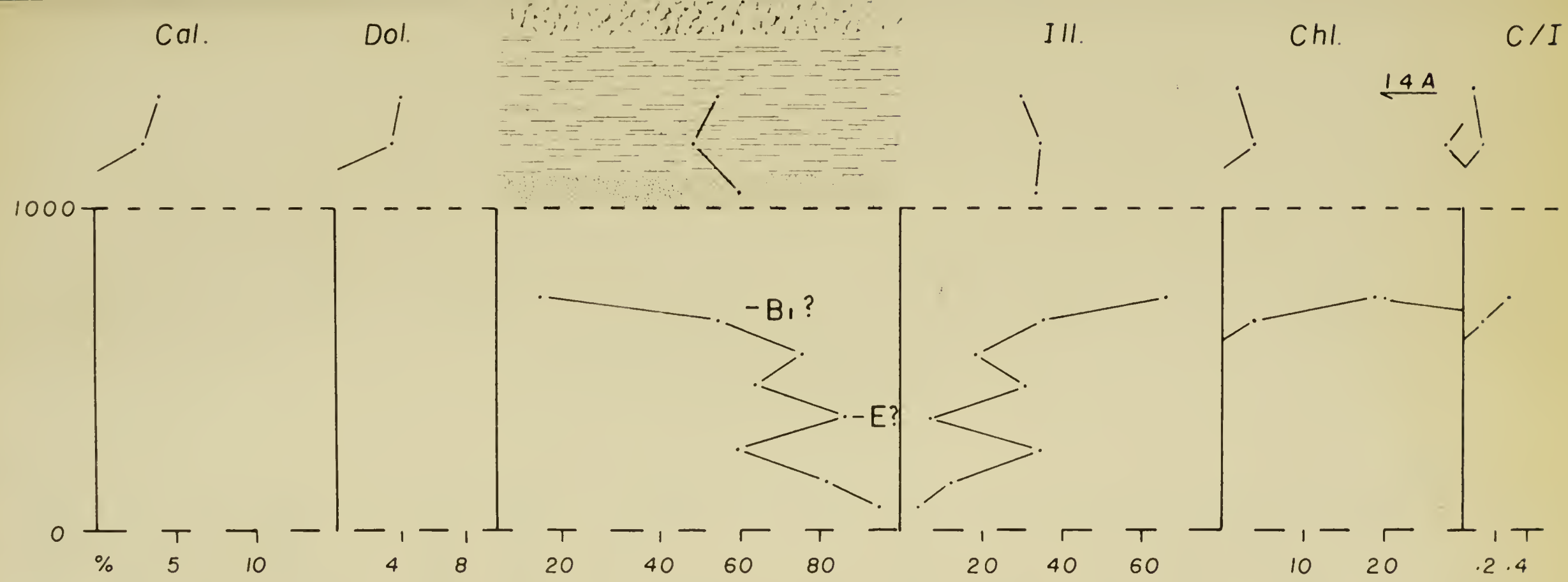
9 - Toad River : Mineralogy

FIGURE 15

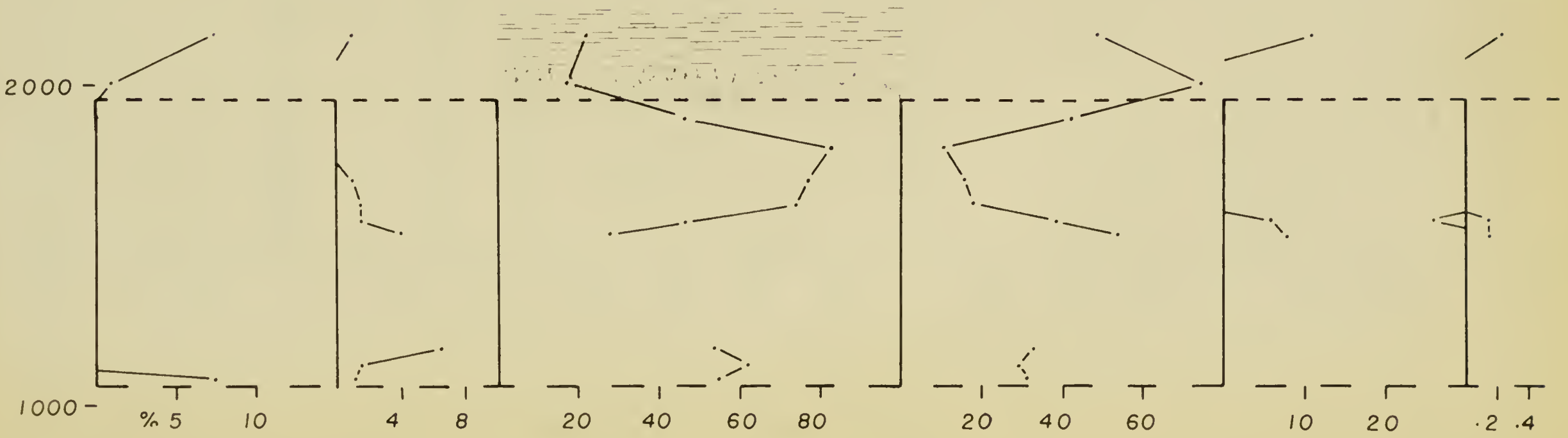


10 - 25 BR 64 : Mineralogy

FIGURE 16

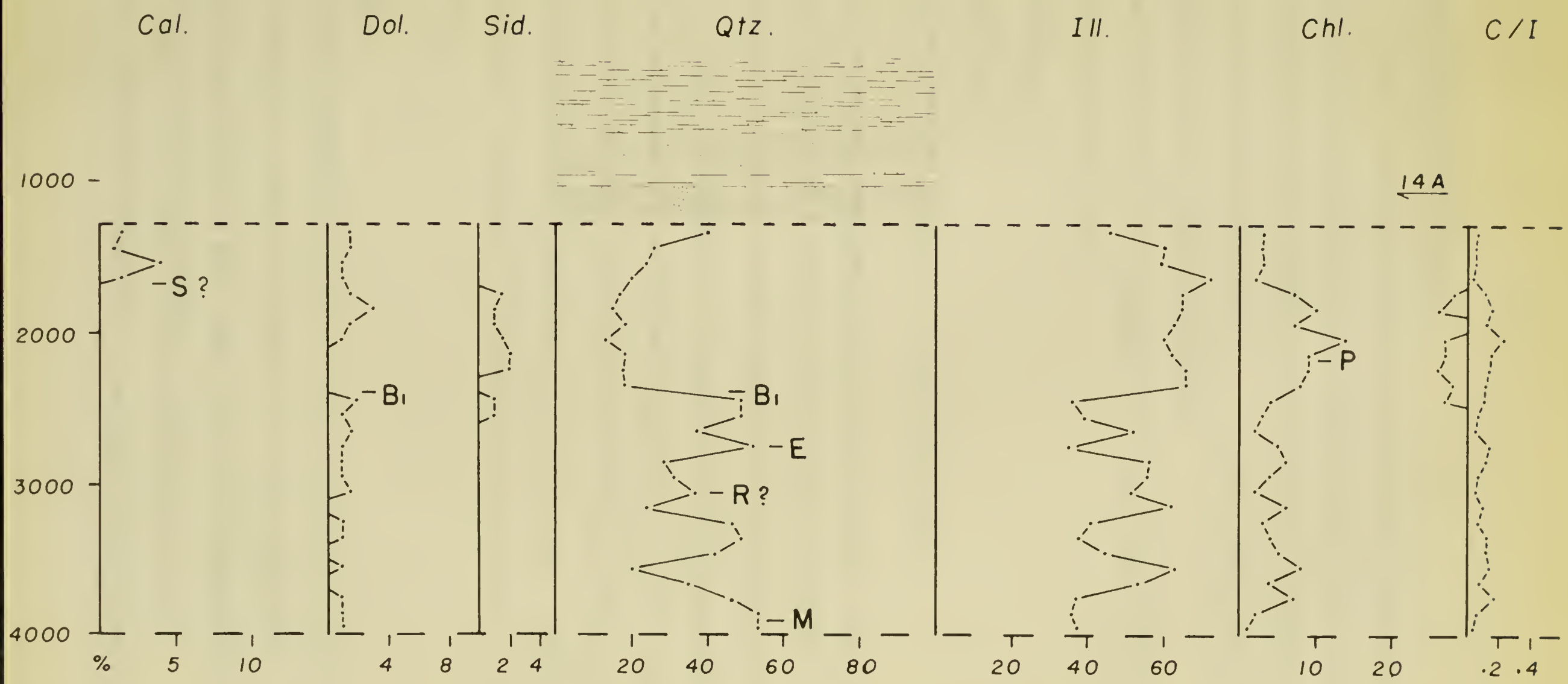


12 - P1-63 : Mineralogy



11 - P3-63 : Mineralogy

FIGURE 17



13 - E. Grayling : Mineralogy

FIGURE 18

Control Point #5 (Beavercrow)-Figure 11.

S - As in Figure 10, except for slight upward shift of the siderite facies.

P - High quartz unit extending above P in previous control point is here correlated with a thick sandstone. Note however the confirmation of the correlation by relative position of the marker near the middle of the sideritic shale unit of both control points.

B1 - Local siliceous shale unit, probably a facies equivalent of the siliceous limestone in Beaver River.

E - As in Figure 10.

R - As in Figure 10.

M? - Dubious; based on high quartz in lowest shale sample.

It will be evident that these correlations vary in quality. Some, such as "X" and "B1" are purely local in character; others, such as "K" and "R", are reasonably persistent but cannot be carried around the complete correlation loop. Markers "S", "E" and "M" are the most characteristic and the most persistent. With assistance from the geochemical correlations, these markers can be carried around the loop to divide the Besa River and its equivalents into Upper Mississippian, Lower Mississippian and Upper Devonian Series and the Givetian Stage. The presentation of these correlations in cross section will be deferred pending discussion of the geochemical data.

E. Petrography

In order to determine the origin and mode of occurrence of some of the mineral constituents, thin sections were prepared from some typical shales, limestones, cherts and sandstones of the study area. Most of these were prepared from drill chips, so that orientation of the thin section relative to bedding is not known.

Plate I shows photo-micrographs of some typical shales from the Besa River

PLATE I

PLATE I

A. Control Point 7 - Evie Lake 89-G; Exshaw Shale @ 3,670'.

X 65. Siliceous sponge spicules and spicule fragments plus radiolarian capsules in matrix of black shale.

B. X 200. Magnified view of radiolarian capsule in top central portion of A. Note spongy silica in upper right hand corner.

C. " 7 - Evie Lake 89-G; Horn River Shale @ 6,600'.

X 65. Calcispheres and unidentifiable calcite debris, spongy chalcedonic quartz in matrix of black shale.

D. " 6 - Fort Nelson 95-J; Horn River Shale @ 6,750'.

X 150. Spores in matrix of light grey shale. Largest spore has a diameter of 27 microns.

E. " 5 - Beavercrow #1; Banff Shale @ 2,780'.

X 65. Mat of partly digested and recrystallized siliceous sponge spicules in black shale matrix.

F. " 4 - Beaver River #A-1; Exshaw Shale @ 8,703'.

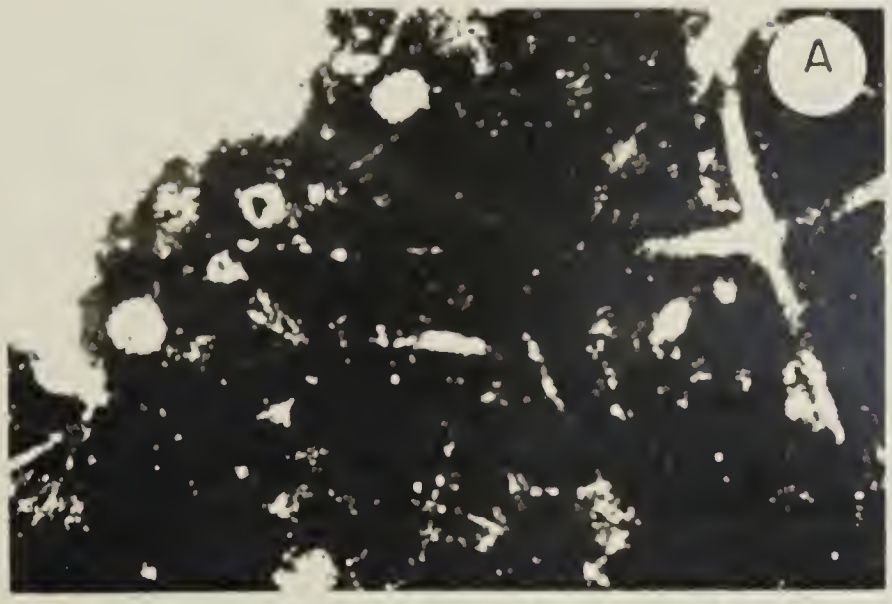
X 65. Radiolarian capsules, spongy chalcedonic silica and small quartz needles which may be radiolarian spicules.

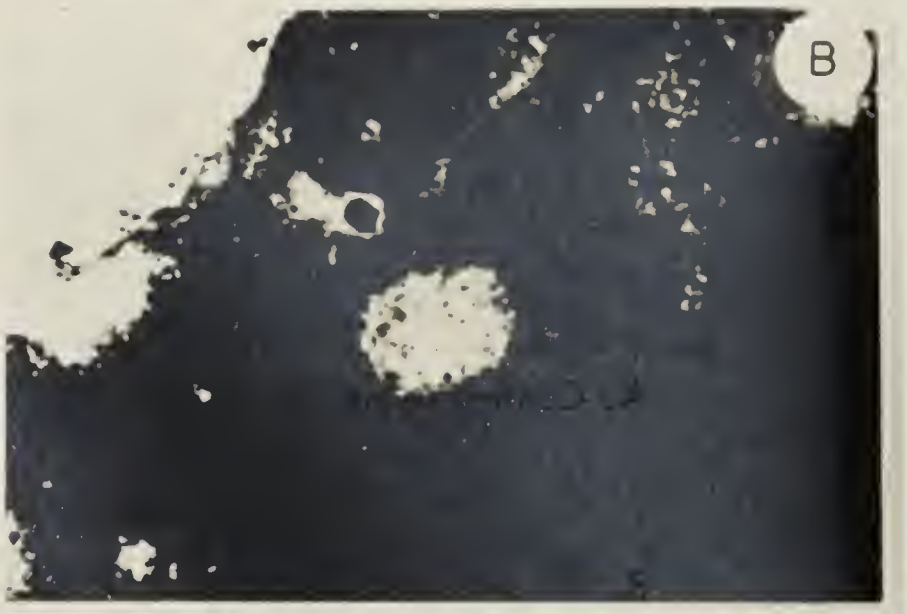
G. " 13 - East Grayling d-95-F; Besa River Shale @ 3,350'.

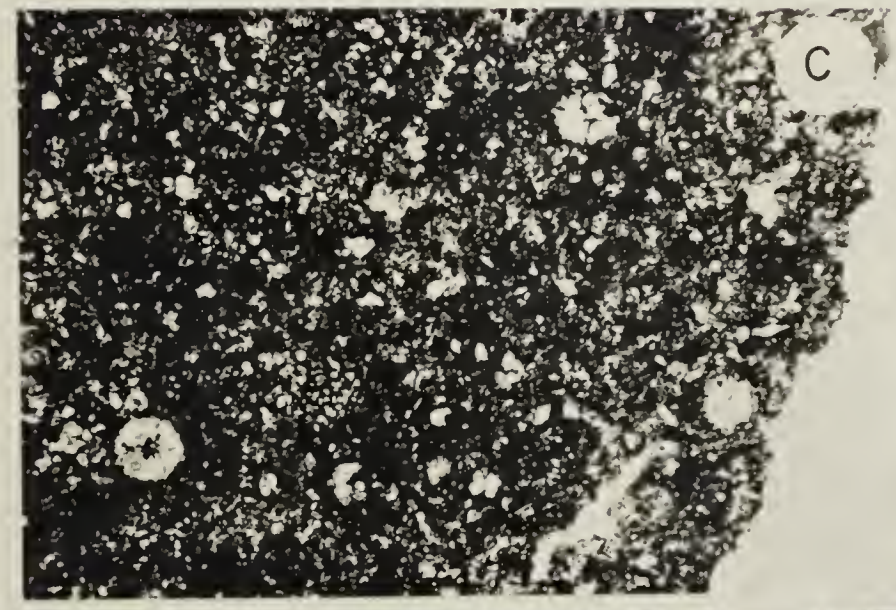
X 65. Lenticles of chalcedonic silica in matrix of black shale.

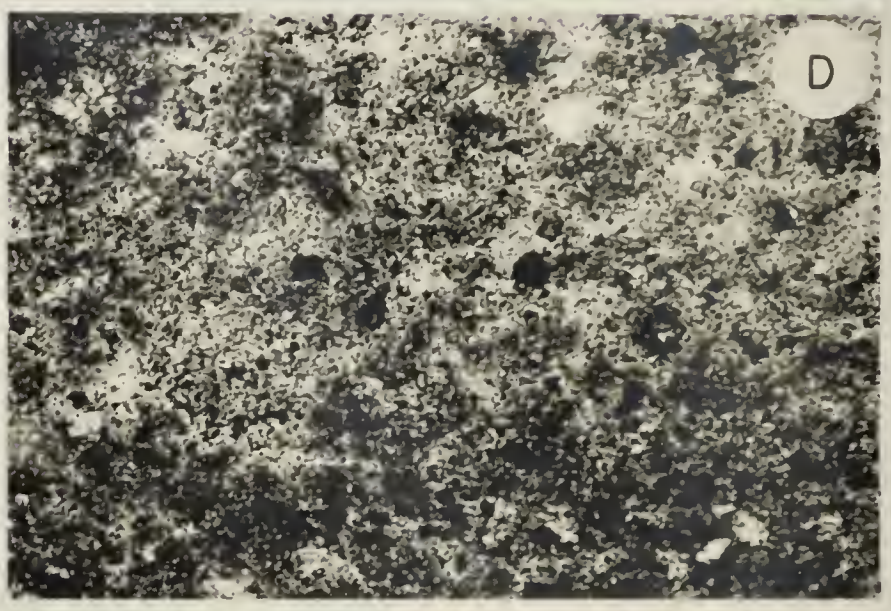
H. " 13 - East Grayling d-95-F; Besa River Shale @ 3,650'.

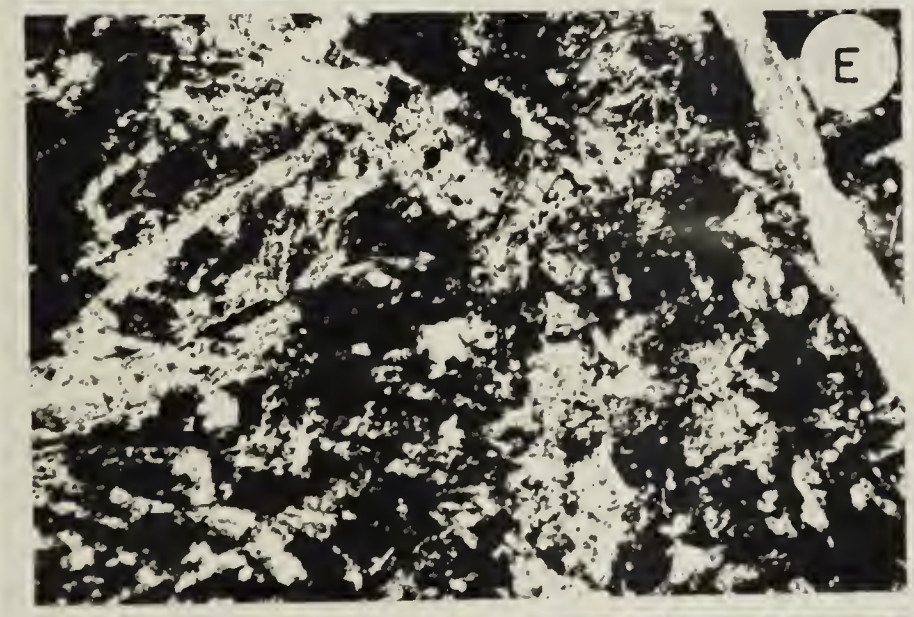
X 65. Corroded calcareous sponge spicule (left) and siliceous sponge spicule (right).

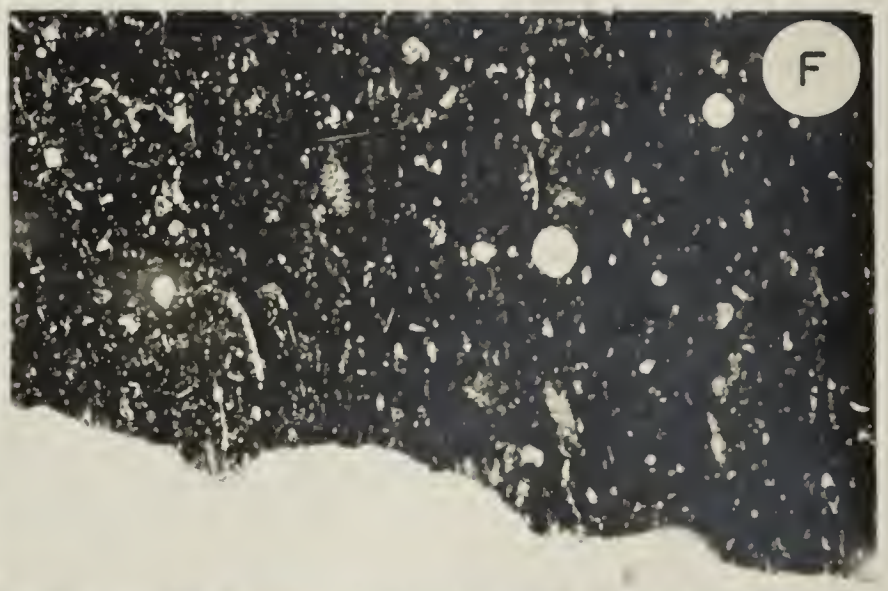












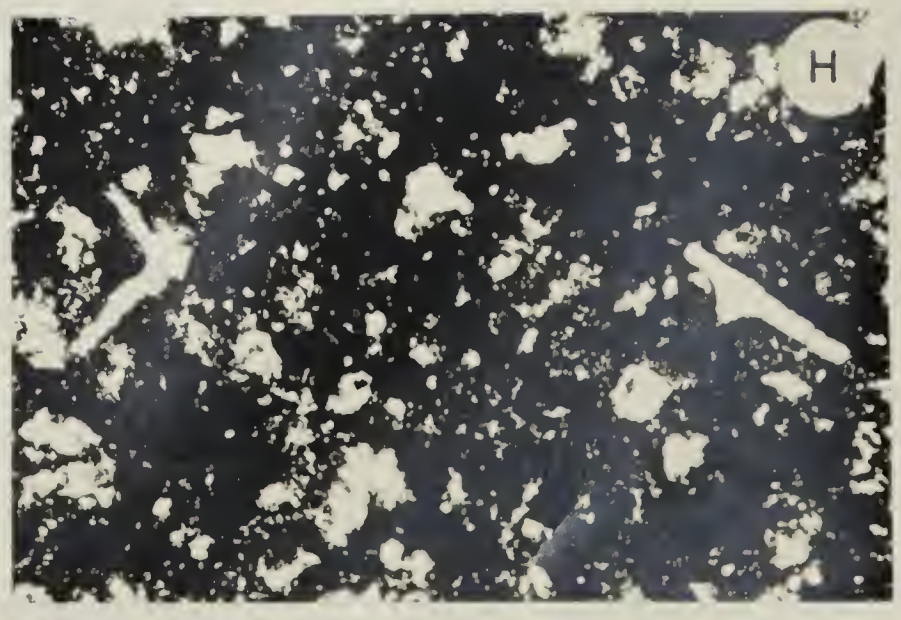


PLATE I.

Shale and lateral equivalents. One pertinent observation concerns the manner of occurrence of quartz, which is present as sponge spicules (Plate I A, E, H), radiolarian capsules (Plate I A, B, F), spongy chalcedonic secretions (Plate I B, C) and "lenticles" of chalcedonic silica (Plate I G). In no instance was any quartz of demonstrably detrital origin observed; many of the smaller particles have an acicular shape which suggests that they may have originated as radiolarian spicules or as microscleres of sponges. Whether the spongy and lenticular chalcedonic material is a true inorganic precipitate or partially resorbed and recrystallized skeletal debris is open to question, but the latter possibility is favoured in view of the high degree of resorption and obliteration of original form evident in Plate I E. Krauskopf (1959) has shown that the solubility of amorphous silica is in the order of 50 - 80 p.p.m. at 0°C, increasing sharply to 360 - 420 p.p.m. at 100°C. Thus resorption and redeposition of opaline debris as chalcedonic quartz would be possible in the immediate post-depositional history and increasingly probable under conditions of burial.

That much if not all of the calcite may also be of organic origin is indicated by Plate I C showing "calcispheres" in all stages of disintegration and by Plate I H showing a highly corroded and partially redissolved calcareous sponge spicule.

Plate I C, in which the largest calcisphere has a diameter of 35 microns, and Plate I D in which the largest spore has a diameter of 27 microns, illustrate the extremely fine grain size and mosaic texture of the shales. These two photomicrographs are representative of the light colored shales of the more easterly control points. All shales in the more westerly control points contain such a high proportion of finely divided black organic matter that no individual mineral grains are observable in the groundmass.

Plate II shows photomicrographs of limestones and cherts within the Besa

PLATE II

PLATE II

A. Control Point 4 - Beaver River #A-1; Banff equivalent @ 8,500'.

X 65. Shaley limestone; most of the calcite appears to be remnants of calcareous sponge spicules.

B. " X 150. Same as above, but with calcite completely recrystallized and intergrown with chalcedonic quartz. Note authigenic feldspar crystals.

C. " 4 - Beaver River #A-1; Exshaw equivalent @ 8,630'.

X 65. Siliceous calcareous shale. Note radiolarian capsules with pyrite infilled nuclei.

D. " X 65. More calcareous phase of above. Calcispheres and sponge spicules (?) in matrix of black shale.

E. " 4 - Beaver River #A-1; Wabamun equivalent @ 9,035'.

X 65. Euhedral dolomite rhombs in matrix of calcareous and argillaceous chalcedonic chert.

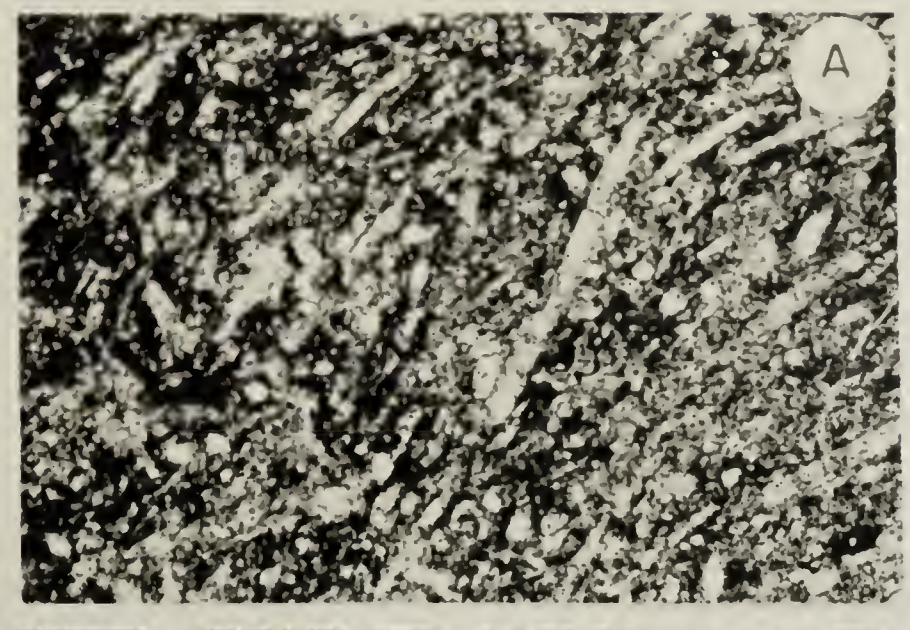
F. " X 65. Crossed nicols. Same slide as above. Quartz veinlet cutting spongy intergrowth of chalcedonic quartz and calcite.

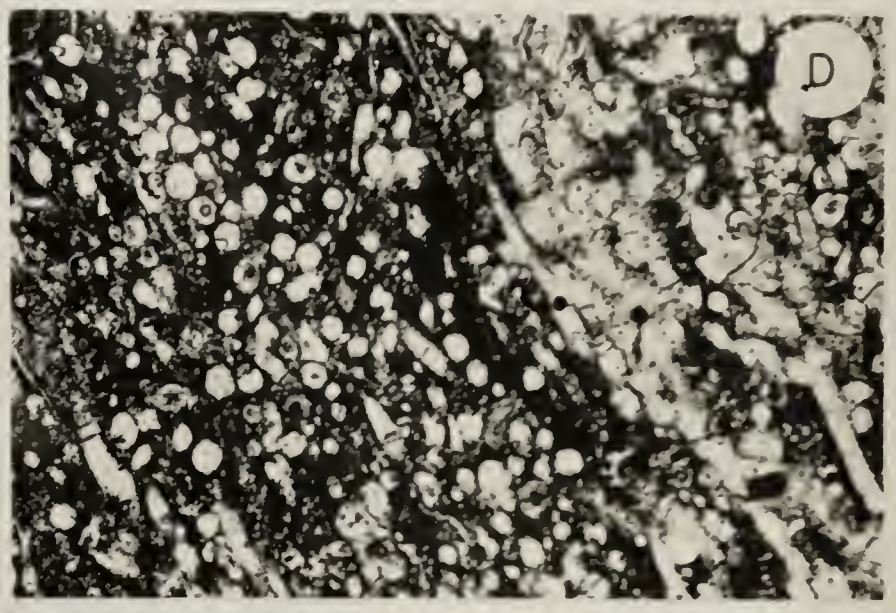
G. " 11 - Surface section P3-63 (Basal Mattson ?).

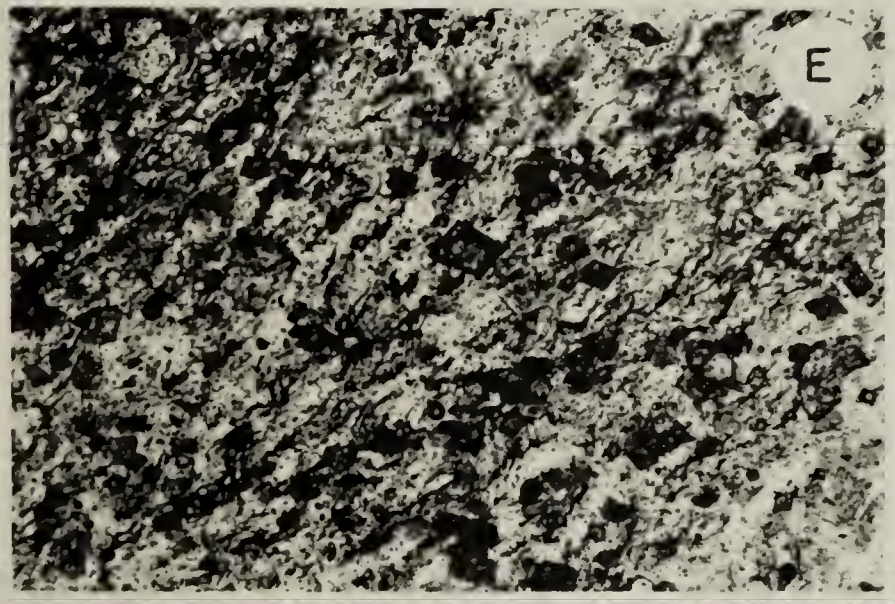
X 65. Calcareous chert. Note shell fragments (ostracods ?).

H. " 11 - Surface section P3-63.

X 65. Crossed nicols. Same calcareous chert. Intimate spongy intergrowth of chalcedonic quartz and calcite. Some rounded quartz grains are probably of detrital origin.







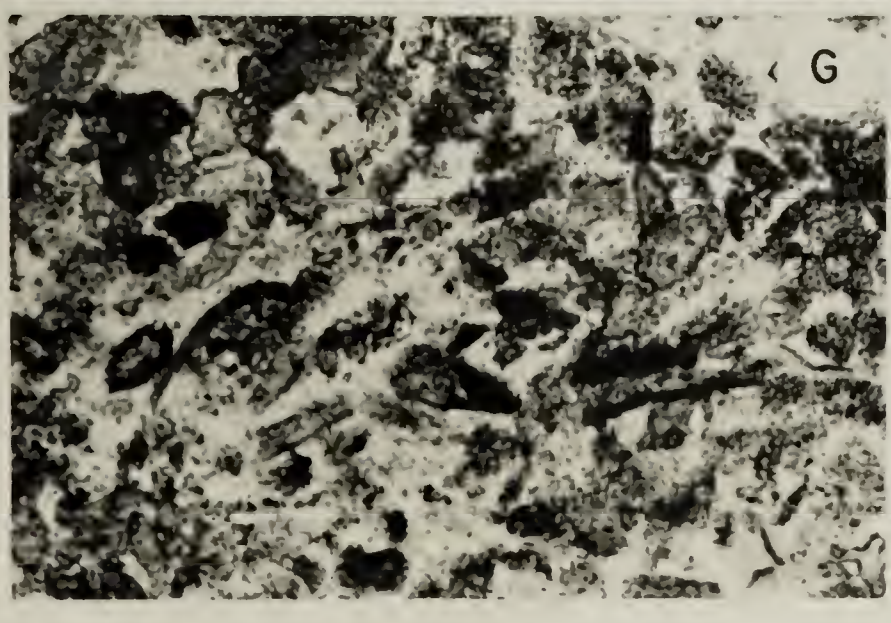


PLATE II.

River Shale. Most of the limestones are highly siliceous and all of the cherts are calcareous, so that these two rock types constitute a gradational sequence. Where re-organization and recrystallization have been minimal, an organic origin is again evident for both calcite (Plate II A, D, G) and quartz (Plate II C). Evidence for organic origin of the quartz is much less obvious than in the shales. Since Krauskopf (ibid) has shown that the rate of polymerization of silica gels from supersaturated silica solutions increases markedly at pH values above 7, it may well be that much of the limestone-associated silica is of inorganic origin.

Plates II G and H offer some slight suggestion of the presence of detrital quartz in the form of small well-rounded grains lacking evidence of organic origin in a matrix of chalcedonic quartz and calcite. This unit, which occurs in surface section P3-63 and is believed to be the correlative of the basal Mattson sandstone, may have originated as a silty siliceous limestone.

Plate III shows evidence of abundant post-depositional precipitation of silica within the sandstone units of the basin. Plates III A, C and D indicate that these sandstones were originally fine to very fine grained, fairly well sorted and porous. Deposition of secondary silica as overgrowths on the detrital grains and as pore filling has produced very hard and non-porous quartzites. In Plate III G this cementation process has been sufficiently late to have entraped some accumulated liquid bitumen. In Plates III F and H the possibility that these sands may have been deposited as turbidites is evidenced by shaly matrix, a suggestion of graded bedding and by "floating" sand grains in a shale matrix.

The very fine grained calcareous sandstone of Plate III C comes from the basal Mattson of control point #9 (Toad River #1), and is believed to correlate with the silicified silty limestone (?) of Plate II G and H, from control point #10 (P3-63). The suggestion of a southward decrease in size of detrital particles offered by this correlation is supported by Harker's (1963) description of the basal Mattson sands of the southwestern Yukon as fine to medium grained.

PLATE III

PLATE III

A. Control Point 2 - Toad River #1; Mattson @ 3,137'.

X 65. Fine to very fine grained sandstone completely cemented by secondary silica overgrowths.

B. " X 65. Crossed nicols. Same as A, showing extent of optical continuity of quartz overgrowths with detrital grains.

C. " 2 - Toad River #1; Upper Besa River @ 3,300'.

X 65. Sandstone, more calcareous and finer grained than above.

D. " X 65. Crossed nicols. Same as above. Note interpenetration of grains.

E. " 5 - Beavercrow; 1,700-1,800'.

X 65. Fine grained sandstone cemented by secondary silica.

F. " 5 - Beavercrow; 1,700-1,800'.

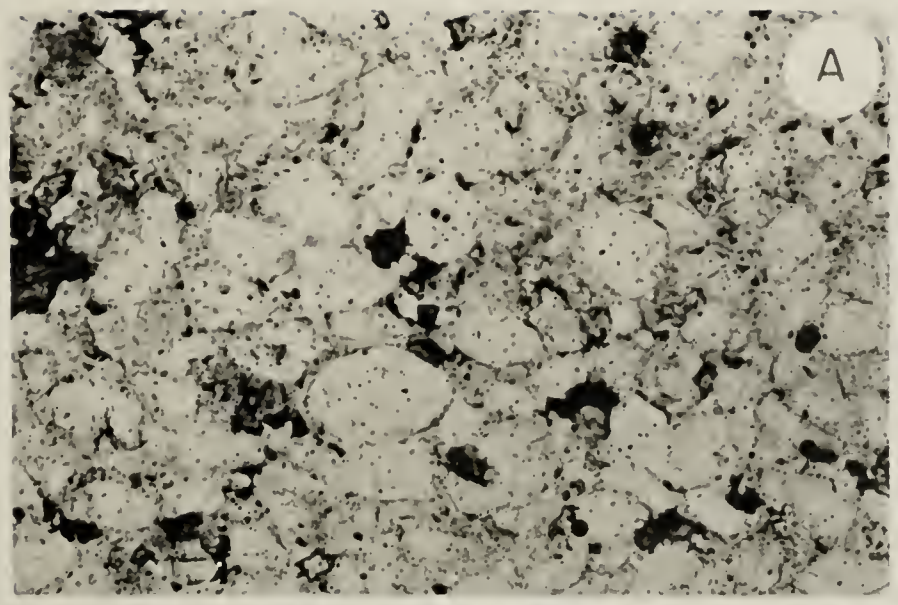
X 65. Shaley sandstone grading into sandy shale.

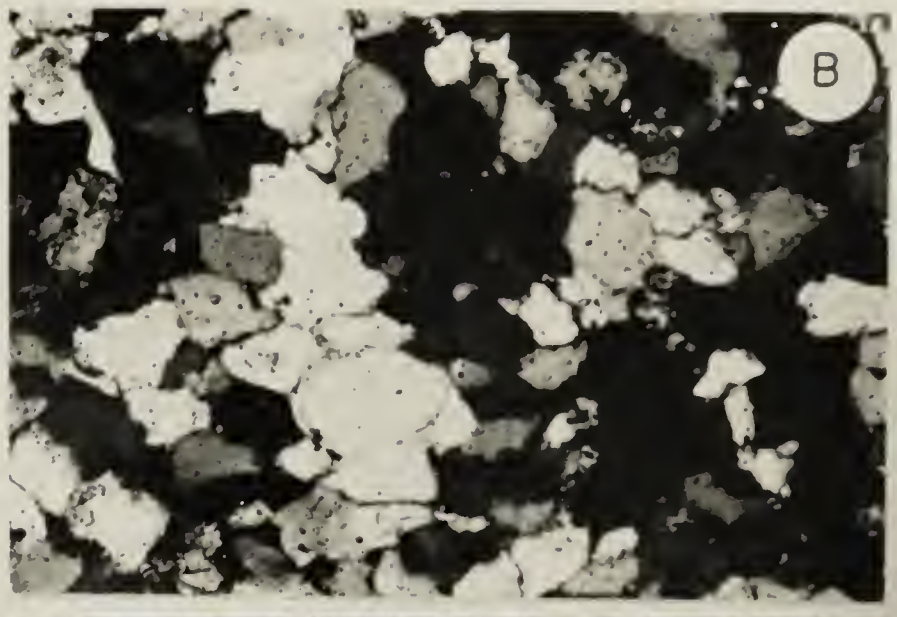
G. " 5 - Beavercrow; 1,700-1,800'.

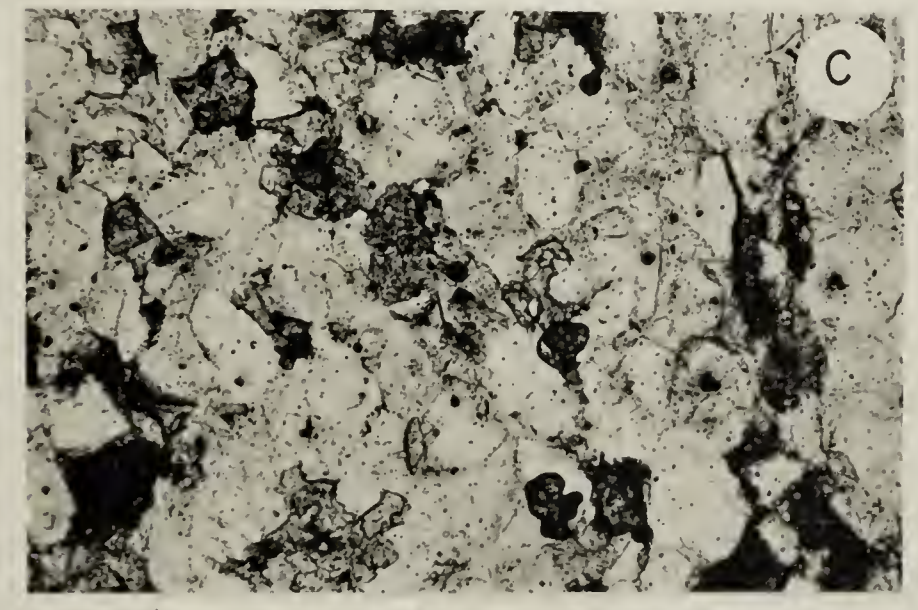
X 65. Bitumen trapped in silicified sandstone.

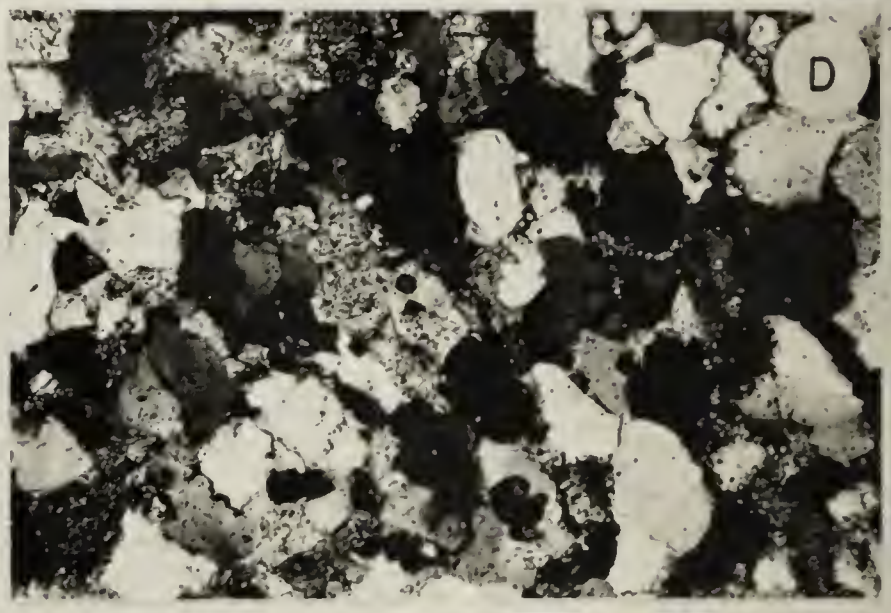
H. " 5 - Beavercrow; 1,700-1,800'.

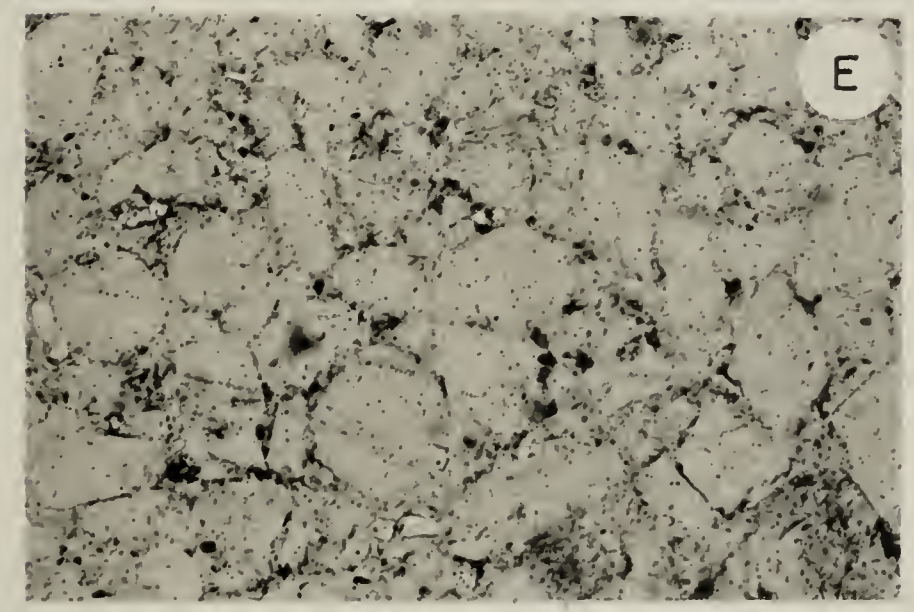
X 65. Shaley sandstone.

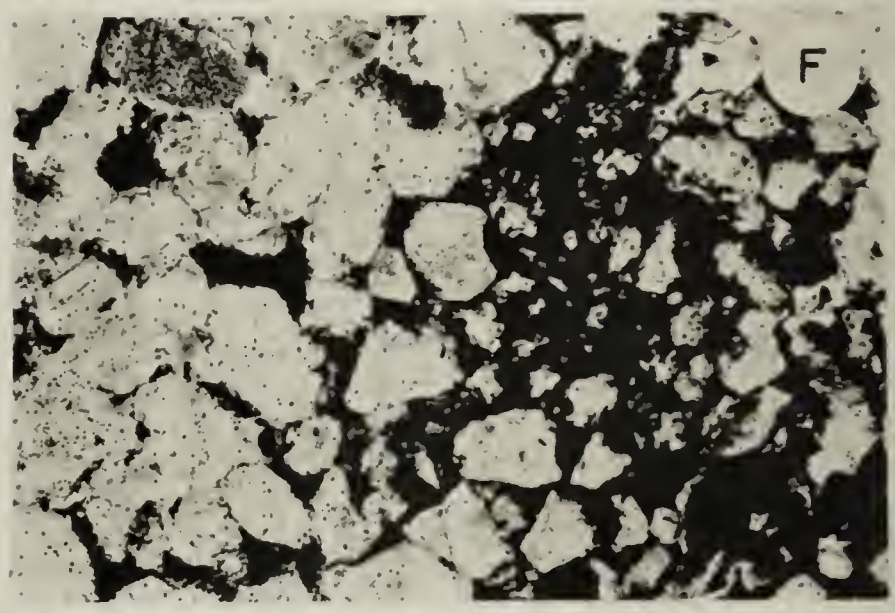


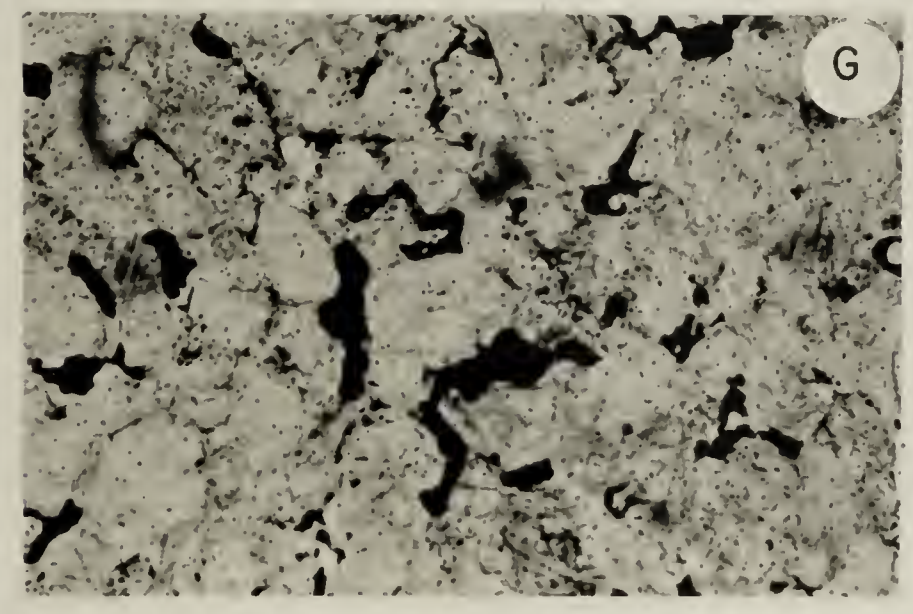












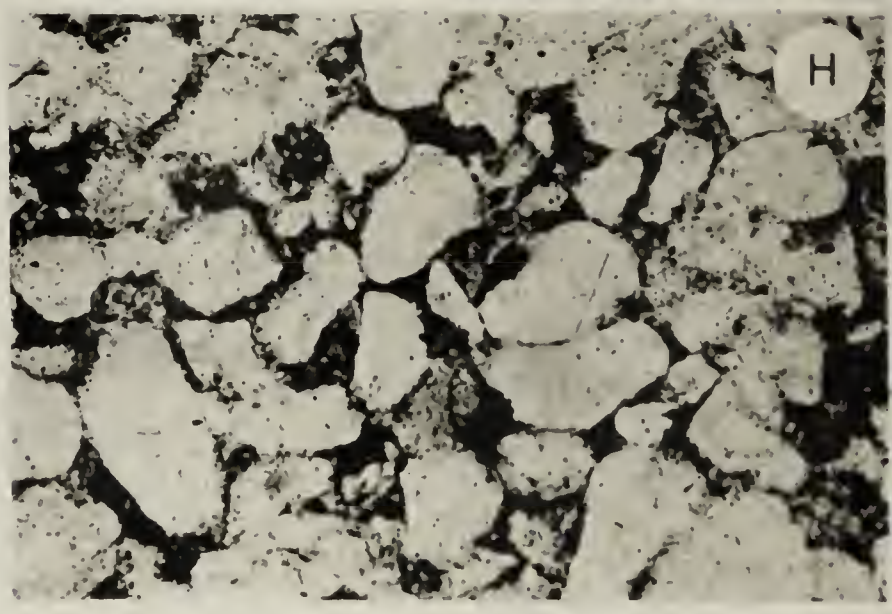


PLATE III.

CHAPTER THREE

GEOCHEMISTRY

A. Techniques

The primary purpose of this phase of the investigation has been to establish chemical variations which might be of value for correlation purposes. Because of the regional scale of the study and the large number of samples, the scope was limited to those elements rapidly determinable by X-ray fluorescence analysis.

Nine elements were investigated: Si, Al, K, Ca, Fe, S, Mn, Sr, and Rb. The choice of these elements was dictated by the desire to provide a check on the mineralogical analyses, by the probability that the most reliable long range correlations would be provided by major oxide variations and by the amenability of these elements to fluorescence analysis. Omission of Na and Mg was dictated by the fact that these elements are not readily determinable by fluorescence analysis at the low levels in which they occur in shales. Combined average MgO and Na_2O content of shales as given by Clarke (1924) is less than four percent.

Analytical determinations were made on a Phillips Norelco Type 12215/0 unit, employing tungsten radiation for all elements except strontium and rubidium, for which a molybdenum source was used. For elements below manganese in the periodic table the analyses were conducted in a vacuum of 0.5 mm. of mercury or less, and pulse height discrimination was employed to limit interference.

As has been indicated in Chapter One, the sample for analysis consisted of a measured volume, approximating one gram in weight, of finely ground powder pressed into a briquet with cellulose backing at a pressure of 30,000 p.s.i. These briquets present a smooth and glossy surface to the incident beam. That the analysed sample was infinitely thick to the X-radiation was ensured by preliminary

comparative studies on a set of briquets in which the volume of powdered shale was varied from 1/3 to 3 times the standard volume. No differences in counting rates were observed on this check set.

Operating procedure involved placing three unknowns and one analysed standard in the sample holder for each analysis. Continued use of the "running standard" provided a check on possible instrument drift as well as a medium for calculating the precision of repeat determinations. The total count on the K alpha peak of each element was obtained for fixed periods of time ranging from 10 seconds for iron to 50 seconds per aluminum. The same count determination was made at a background position and the count above background for the element determined by difference of the two counting rates. Four chemically analysed shale standards were used to produce calibration curves for conversion of counting rates to weight percent for each element. The major elements have been reported as oxides.

It was found that the working curves derived from the analysed standards were smooth and relatively linear for most of the elements. For silicon and aluminum however, this was not the case and it was evident that variations in mass absorption co-efficient were playing a significant role in the observed counting rates. To obviate this difficulty a computer program was devised for correction of the observed counting rates for variations in mass absorption co-efficients for silicon and aluminum radiation. In this program the K_2O, CaO and Fe_2O_3 determinations provided by the working curves were accepted. These, plus a first approximation of the SiO_2 and Al_2O_3 from the working curves, were used to compute a first approximation of the mass absorption co-efficients of the sample from known mass absorption co-efficients of the oxides as given by Liebhafsky, Pfeiffer, Winslow and Zemany (1960). The first approximations of the mass absorption co-efficients were then used to provide a first correction to the observed counting rate and second approximations for Al_2O_3 and SiO_2 were determined. This procedure was reiterated by computer until

successive adjustments to the counting rate fell within the predetermined standard deviation for successive runs on the same sample. Further details of the computation procedure and examples of calibration curves are provided in Appendices B and C respectively.

Strontium and rubidium were determined using the matrix correction method of Reynolds (1963) whereby the unknown is corrected for mass absorption by means of the counting rate on the Compton peak. The standard employed for these elements was the granite G-1. Values of 250 p.p.m. for strontium and 220 p.p.m. for rubidium, as reported by Fleischer and Stevens (1961), were accepted.

Standard deviations and precision as calculated from repeat runs on the analysed standards are shown in Table III. In Table IV, a comparison is made between chemical analyses as reported by the U.S. Geological Survey on three Cretaceous shales and one muscovite and X-ray fluorescence analyses on the same samples using the techniques of this report. With two exceptions, high SiO_2 in P259533 and low Al_2O_3 in P207, the results compare favourably with the deviations indicated by Fleischer and Stevens (1961) for inter-laboratory comparison of chemical analyses on the samples G-1 and W-1. Since the standards employed for construction of calibration curves were analysed in the rock analysis laboratories at the University of Alberta, Table IV will include differences arising from inter-lab chemical comparison as well as differences between chemical and X-ray fluorescence analyses.

To avoid the variable of inter-lab chemical comparison, two of the four standards analysed at the University of Alberta were used to prepare calibration curves for fluorescence analysis of the other two standards. This direct comparison of chemical and X-ray fluorescence analyses is shown in Table V.

Table III. Standard Deviation and Precision From Repeat Runs

Constituent	Standard	Amount Present	Standard Deviation	Precision
SiO_2	R 57	53.65 %	± 0.28 %	± 0.52 %
Al_2O_3	R 56	10.27	0.09	0.86
K_2O	R 56	2.00	0.02	1.05
CaO	R 56	1.26	0.02	1.76
Fe_2O_3	R 56	3.30	0.008	0.23
S	R 66	1.32	0.026	1.95
Mn	R 66	0.015	0.0007	4.86
Sr	G-1	250 p.p.m.	5 p.p.m.	2.04
Rb	G-1	220 p.p.m.	2 p.p.m.	0.96

Table IV. Comparison of Fluorescence Analyses to U.S.G.S. Chemical Analysis

	P259533 (shale)		P259563 (shale)		P258491 (shale)		P207 (muscovite)	
	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray	Chem.	X-ray
SiO_2	62.8	67.8	64.6	64.1	68.4	67.0	47.1	47.6
Al_2O_3	8.36	8.49	14.10	13.40	13.90	15.03	31.28	28.60
K_2O	1.21	1.12	0.36	0.30	2.40	2.31	10.43	10.38
CaO	3.07	2.44	0.81	0.66	0.33	0.25	0.09	0.06
Fe_2O_3	4.20	4.57	3.27	2.87	5.06	4.60	4.86	4.15

Table V. Comparison of Fluorescence Analyses to U. of A. Chemical Analyses

	R 66		R 67	
	Chem.	X-ray	Chem.	X-ray
SiO_2	58.03%	59.15%	54.26%	52.80%
Al_2O_3	17.31	17.28	5.55	6.24
K_2O	2.24	2.20	0.80	0.80
CaO	0.84	0.90	16.98	17.10
Fe_2O_3	5.14	5.80	1.49	1.50

This internal comparison indicates very gratifying agreement between the chemical and fluorescence analyses.

B. Distribution of Major Oxides

From the point of view of the stratigrapher, the possibility of element distribution in a particular lithologic end member as a function of time is an appealing one. Considering the evidence of gradual evolution of the hydrosphere (Rubey, 1955), and considering in addition evolutionary changes in the biotic assemblages which have, as demonstrated in Chapter Two, contributed heavily to the shale lithotype, the possibility of time-dependent elemental distribution may deserve more attention than it has as yet received. The well known and very marked variation in the ratio of calcium to magnesium (cf. Fairbridge, 1957) is one such example of a time-dependent variation.

Vinogradov and Ronov (1956) have noted a number of time-dependent changes in the Phanerozoic shales of the Russian platform. They demonstrate a gradual decrease in K_2O with decreasing age, an increase in CaO, and a slight decrease of Al_2O_3. The most striking time dependent behaviour is shown by K_2O, which decreases from more than 4.5% in the Cambrian to about 2% in the Cretaceous.

Recently Tourtelot has shown that the average of a number of other

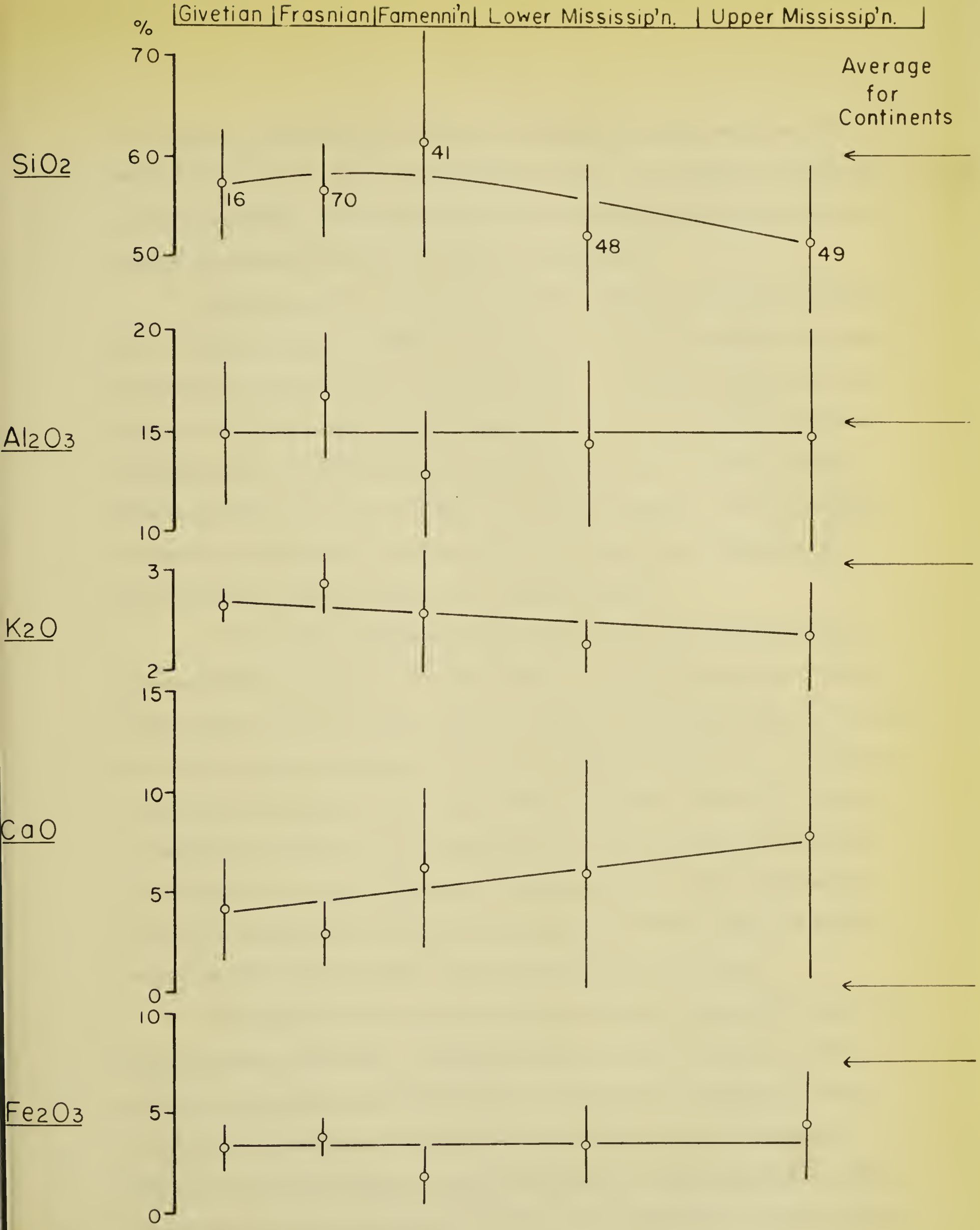
shale analyses fit the same general pattern of increasing K_2O content with increasing age.

Figure 19 is intended to evaluate the time dependence of the major oxides investigated in this study. The evaluation is restricted to those control points for which the conventional or mineralogical correlations are regarded as highly reliable. The averages of all samples within a given stage or series have been plotted as a function of time, together with the computed standard deviation from the mean, and a best fit line has been drawn to indicate the tendency to time dependence. The number of samples included in each mean value is indicated beside the plotted points, and the continental crustal average as indicated by Mason (1952) for each oxide is also shown. Large standard deviations indicate a high degree of geochemical facies dependence which will, of course, render the evaluation of time dependency more difficult.

It will be noted that the oxides SiO_2, K_2O and CaO show some suggestion of time dependency. The direction of variation for the latter two is the same as that observed by Vinogradov and Ronov. The variation in Al_2O_3 noted by them is not evident here however, whereas there is a time dependency for SiO_2.

The limited time base and comparatively limited area of the present study does not justify the erection of elaborate hypotheses to explain the observed time dependent variations. It will suffice to mention that Vinogradov and Ronov have invoked the shrinking exposure of crystalline K_2O-rich rocks to explain the variation in that oxide. Expansion in numbers of calcite secreting pelagic organisms could explain the CaO variation, and an opposed trend among the SiO_2 secreting organisms would not be implausible.

Whatever the significance of the time-dependent variations of the major oxides, these variations are certainly not sufficiently marked to provide a "signature" for any particular series or stage. To further evaluate the correlation possibilities of the major oxides and of sulphur, their variance has been plotted as a function of depth for each control point. The resulting plots are presented in Figures 20 through



Major Oxides Vs. Time

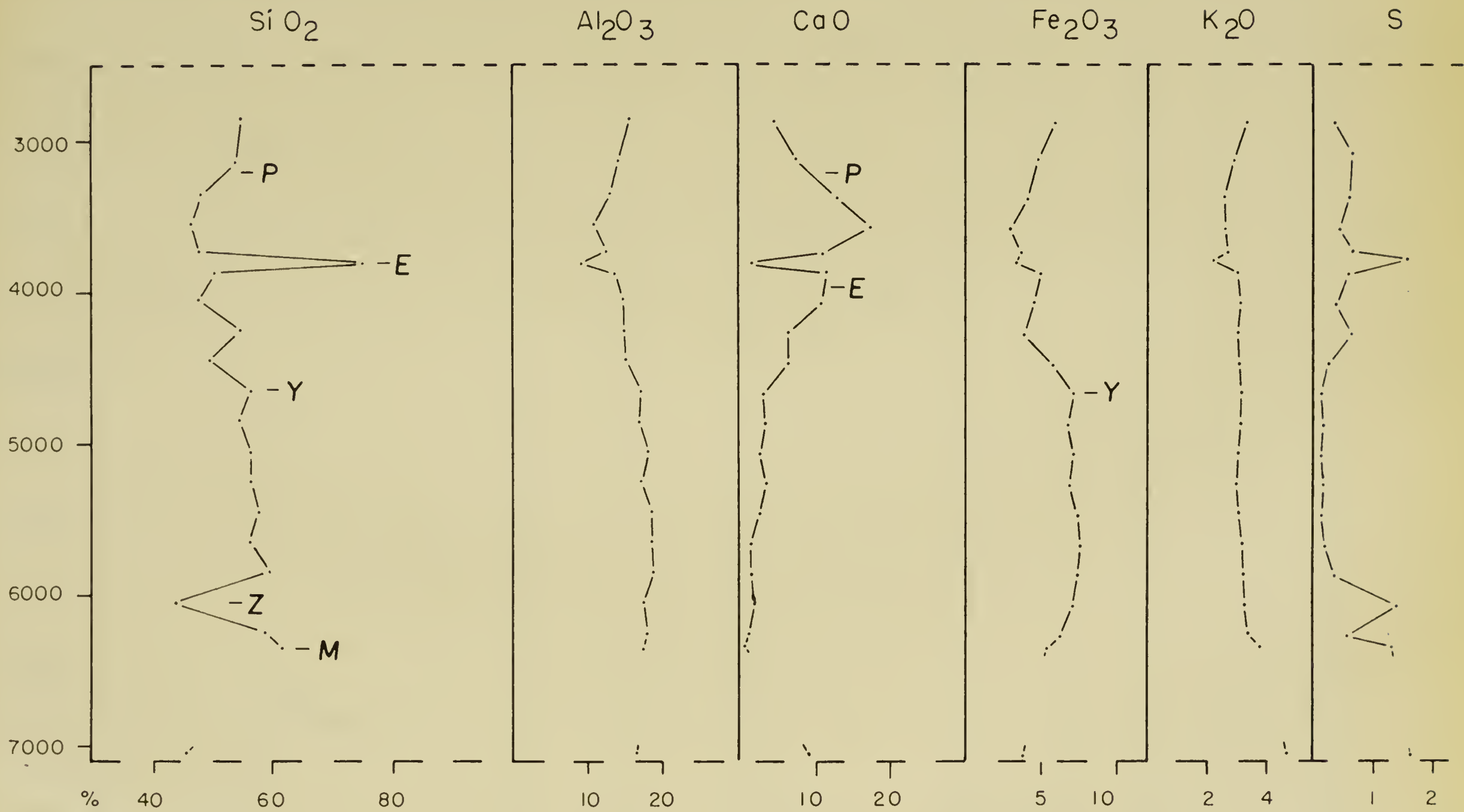
FIGURE 19

31, arranged in the same order as Figures 7 through 18. Correlation points on the major oxide logs have again been indicated by letters. In most cases the correlation points are coincident with those derived from the mineral logs, but some additional markers, for the most part local in character, are observed.

The major oxide curves provide excellent confirmation of the mineralogical data. Comparing Figures 7 and 20, for example, we see that the shape and character of the calcite and CaO curves is virtually identical. The shape of the chlorite and Fe_2O_3 curves is also closely comparable and, in the absence of a close correlation of Fe_2O_3 with S, this tends to confirm identification of the 7 Å peak as chlorite. Quartz and SiO_2 curves are very similar, as might be expected. It has already been noted that the comparison of SiO_2 to quartz is sufficiently close to eliminate the possibility of any significant amount of amorphous material.

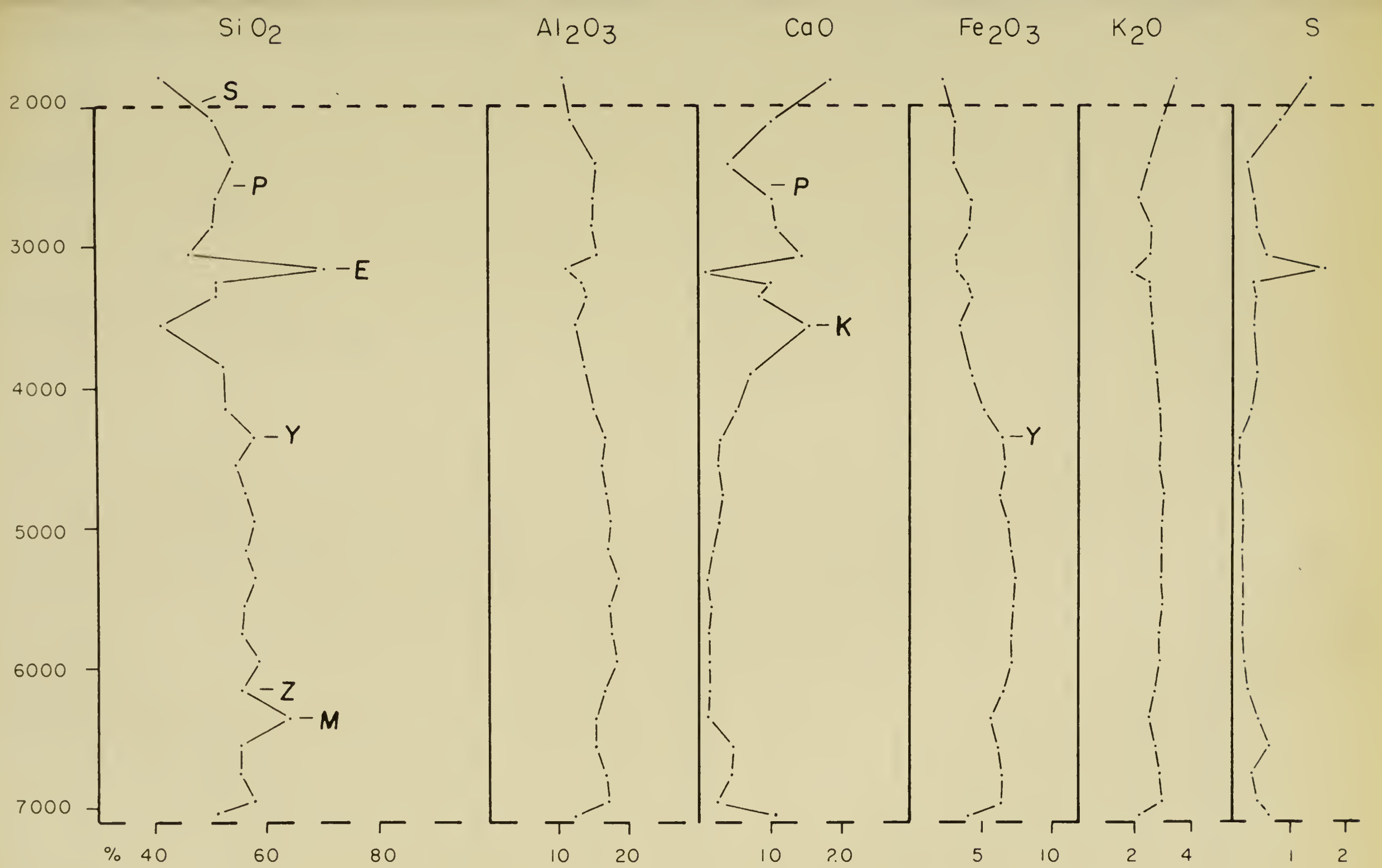
In the surface control points (Figures 29 and 30) some weathering effect is apparent despite the care taken to select apparently unweathered material. Notably, sulphur content of these sections is very low compared with adjacent subsurface control, and the iron content also appears to have been depleted to some extent. The calcium oxide content also appears rather erratic in these localities. Certainly this evidence of weathering is sufficient to have affected the correlation possibilities of both the mineral logs and the major oxide logs. It is gratifying that a number of markers are still clearly recognizable at the Besa River type section 25BR64 (Figures 16 and 29), the most notable being the Exshaw which is quite obvious on both logs.

A comparison of the correlation value of the mineral logs and the major oxide logs is pertinent at this point. As already indicated, most of the major correlation points are recognizable on both types of log. In particular, the radioactive shale units Exshaw (E) and Muskwa (M) stand out quite clearly and on the basis of their high quartz and pyrite (sulphur) content and deficiency in other minerals and oxides, they can be extended well beyond the limits of excess radioactivity and color contrast



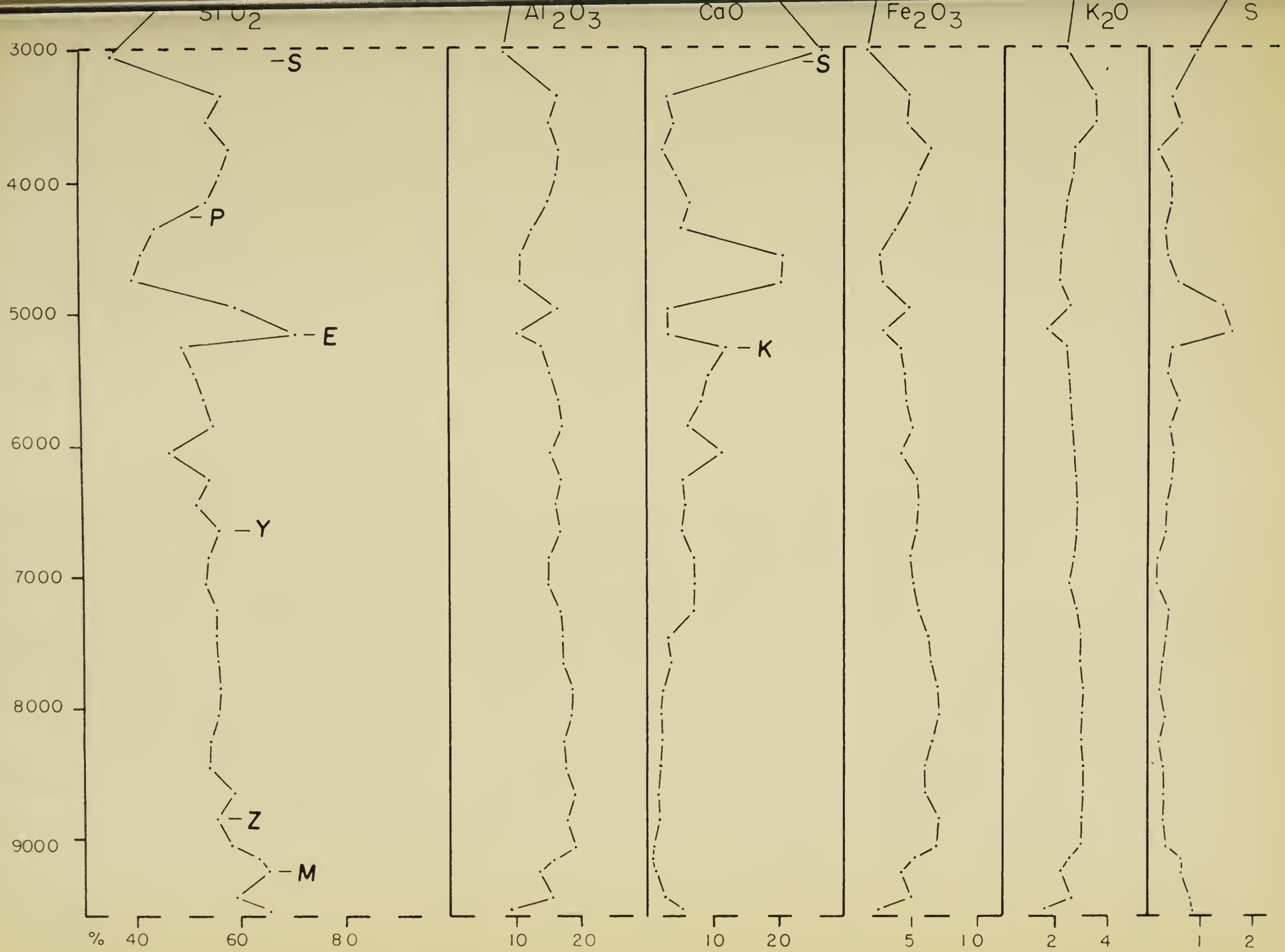
1- Clarke Lake c-94-L:Major oxides

FIGURE 20



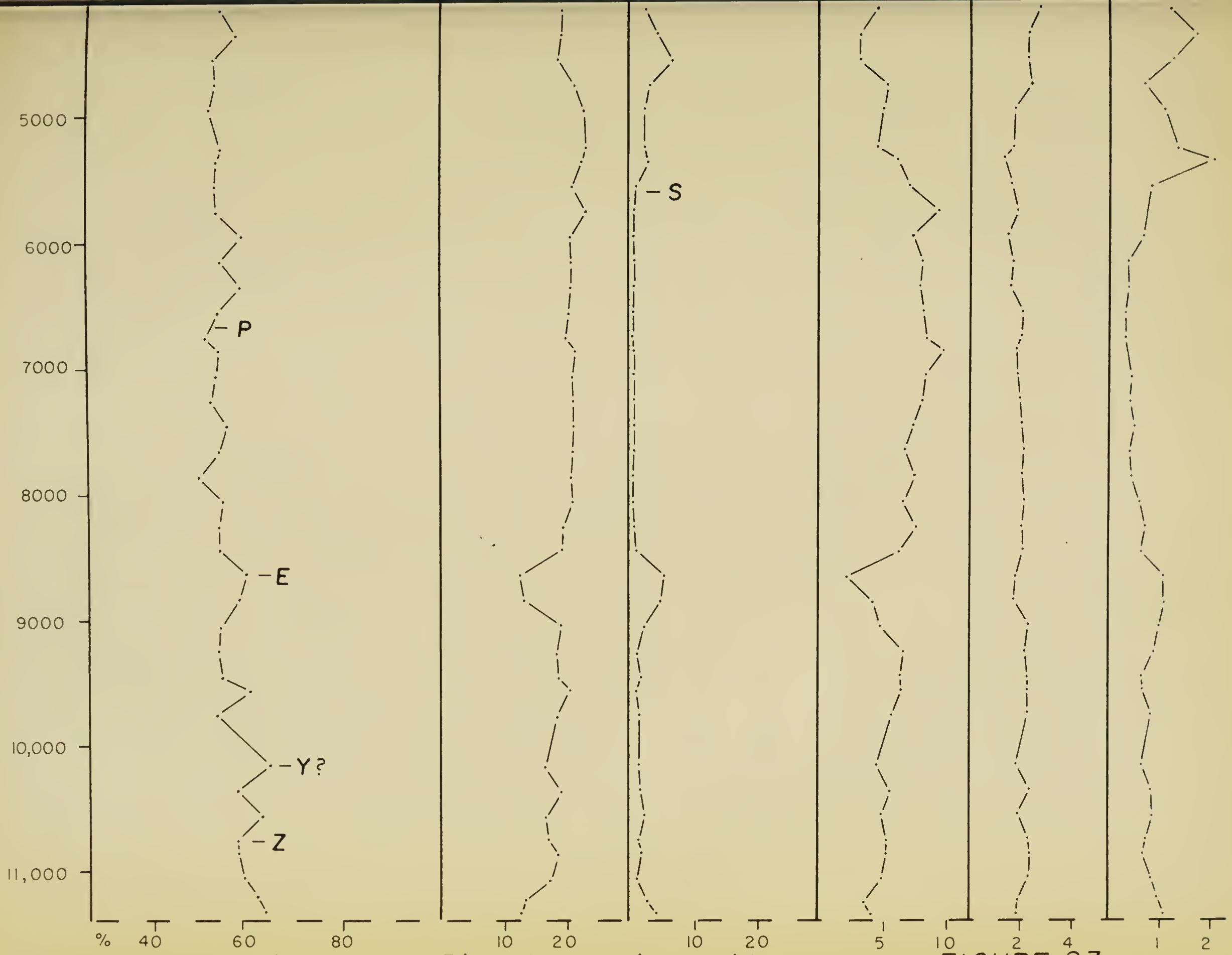
2 - Snake River A-1 : Major oxides

FIGURE 21



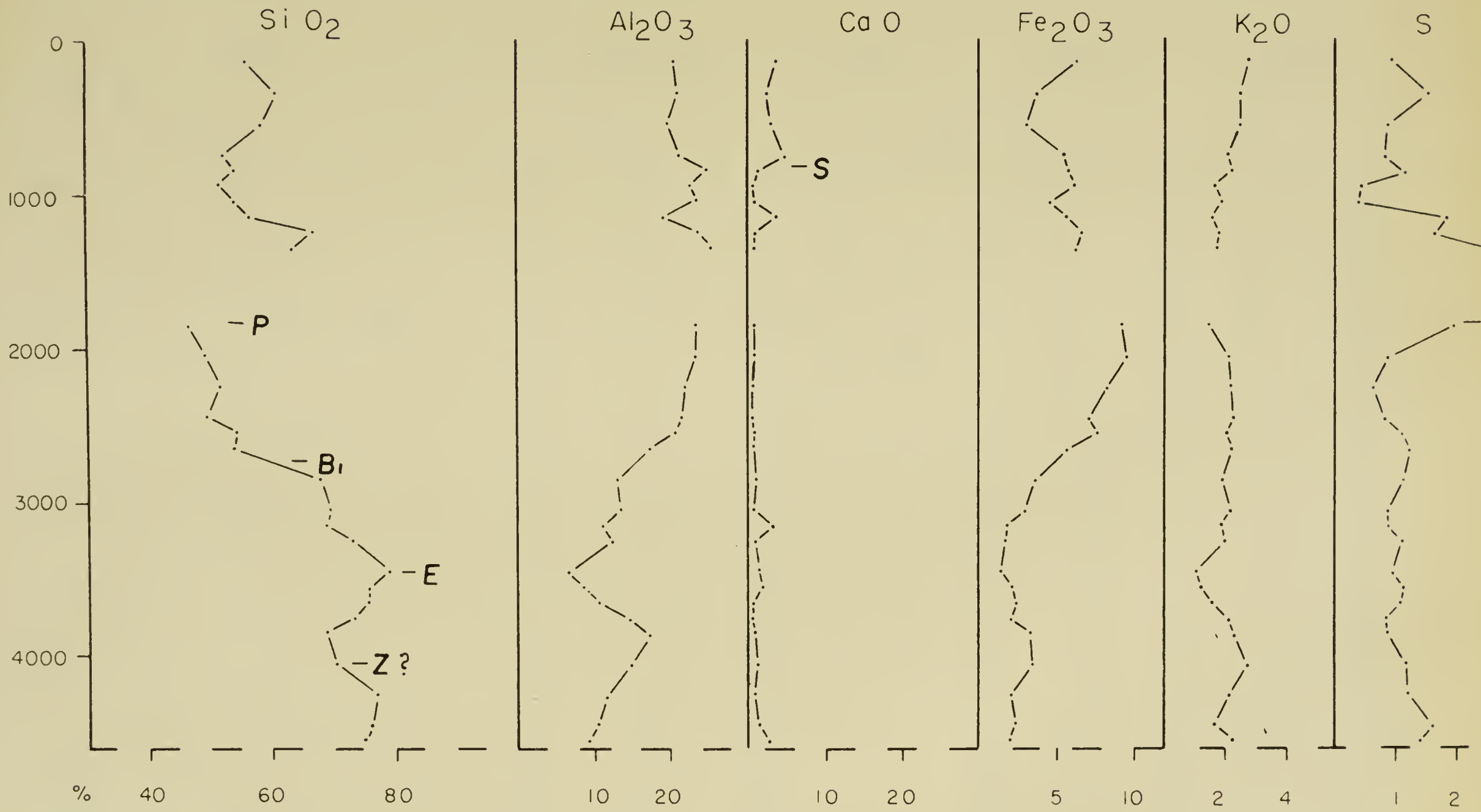
3 - Deer Lake A-1 : Major oxides

FIGURE 22



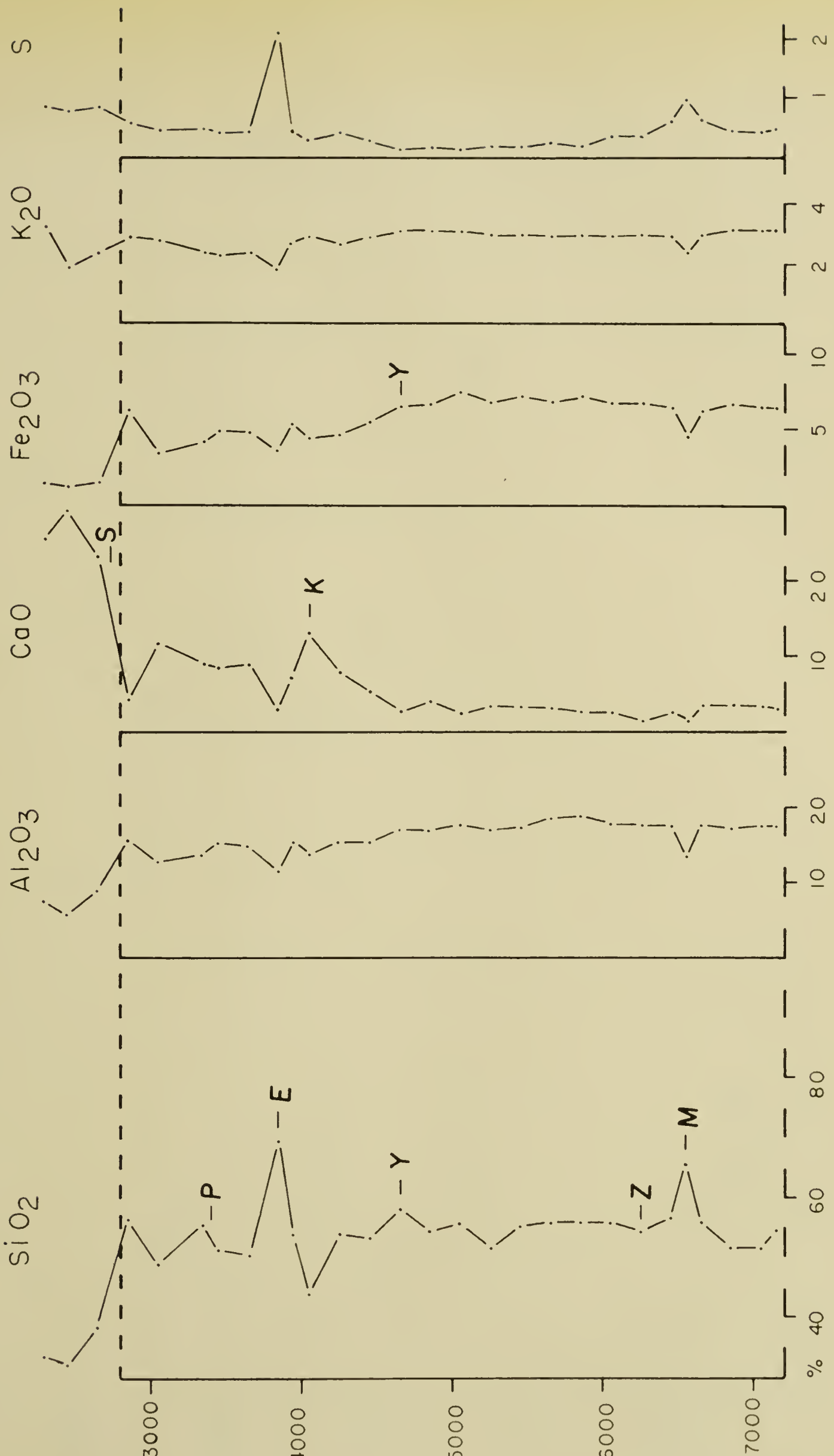
4 - Beaver River A-1: Major oxides

FIGURE 23



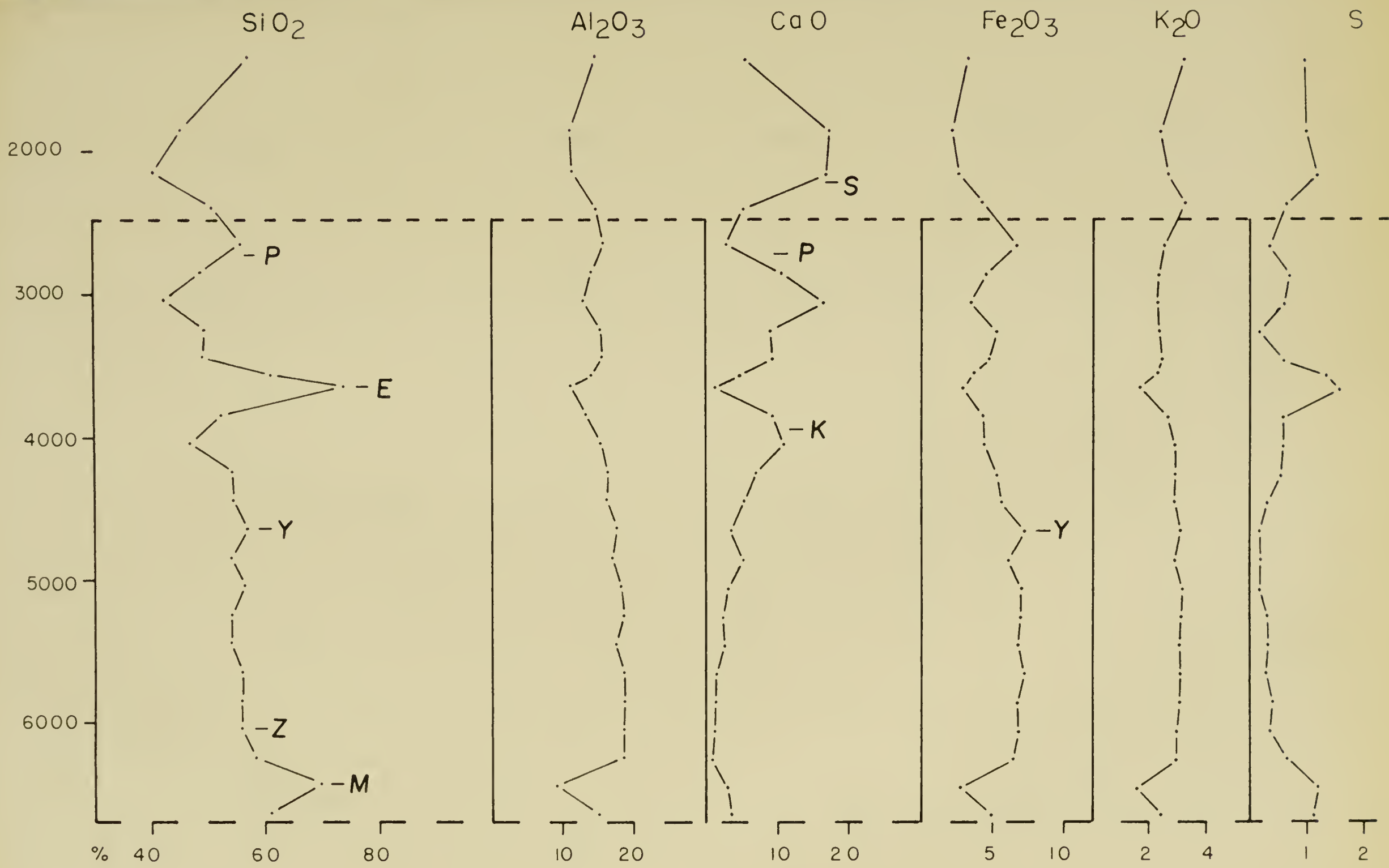
5 - Beavercrow : Major oxides

FIGURE 24



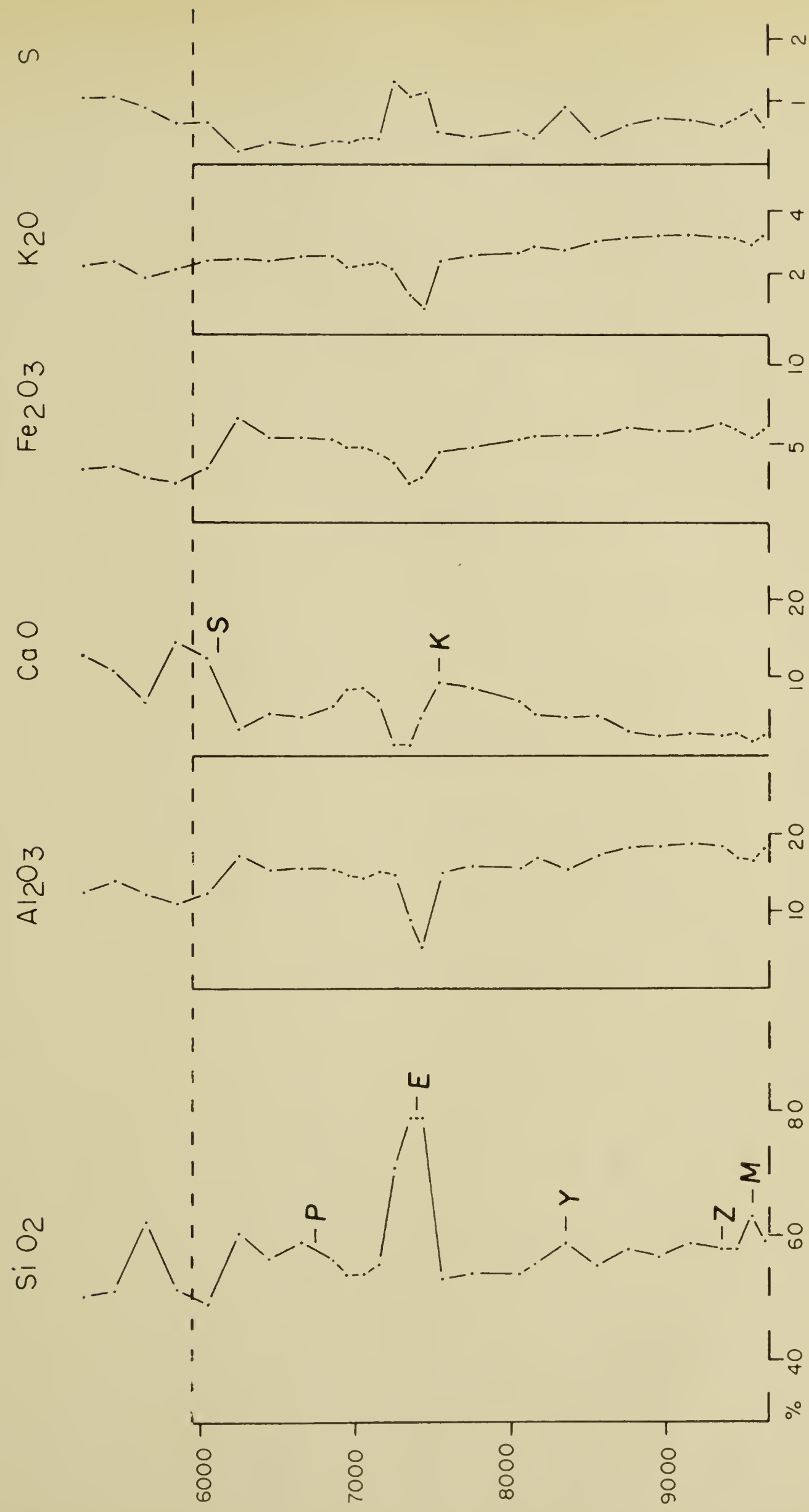
6 - Ft. Nelson # 2 : Major oxides

FIGURE 25



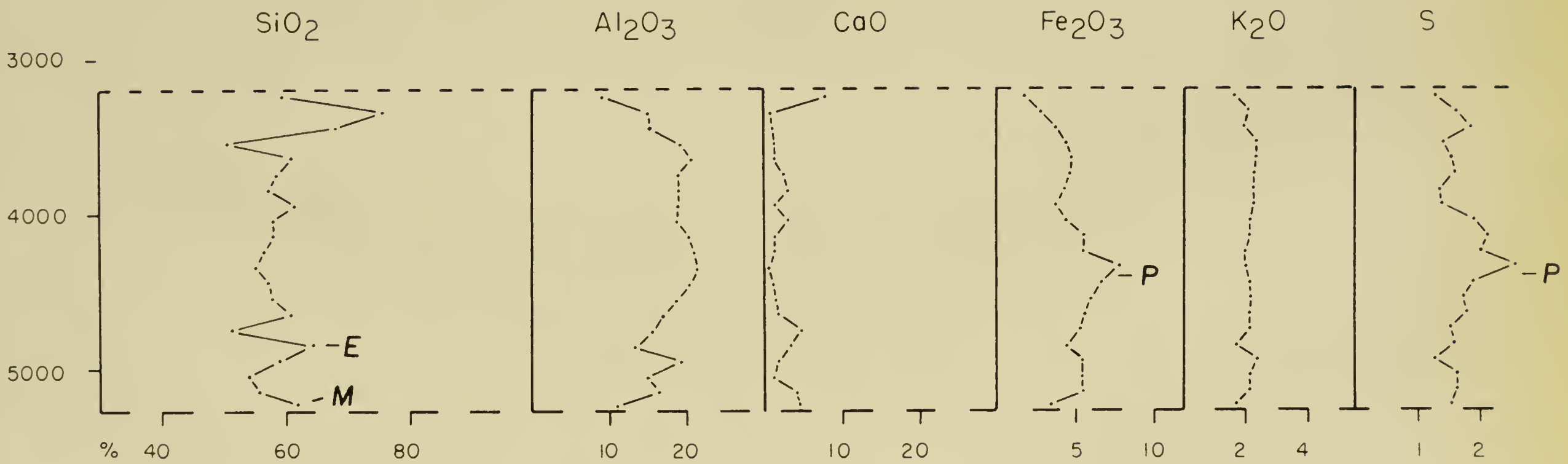
7- Evie Lake #1 : Major oxides

FIGURE 26



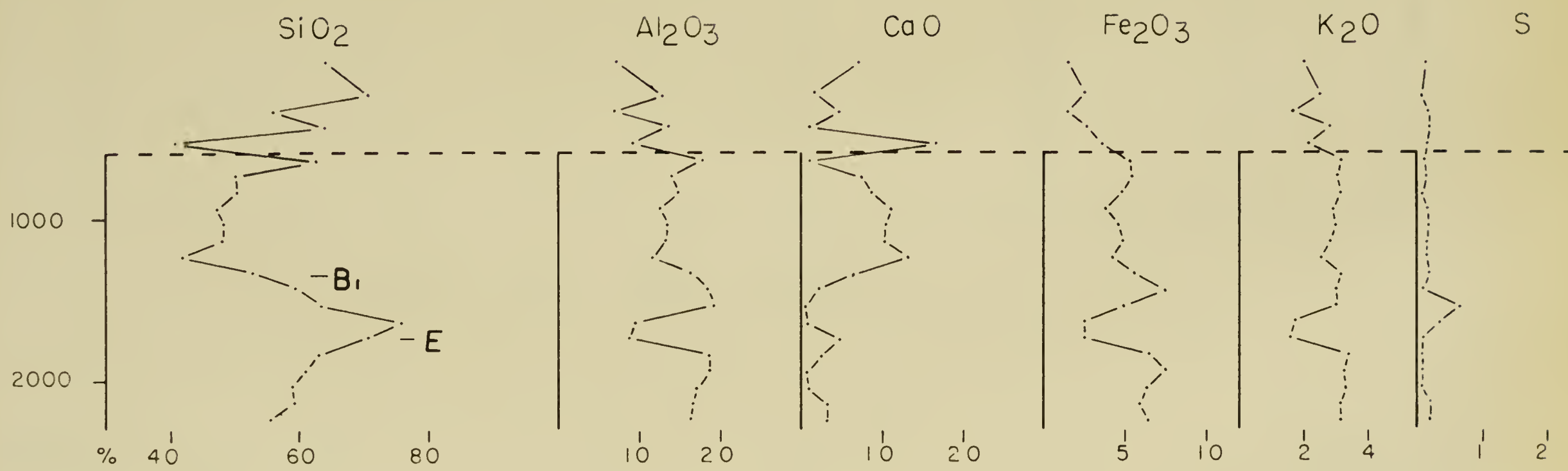
8 - Kledo : Major oxides

FIGURE 27



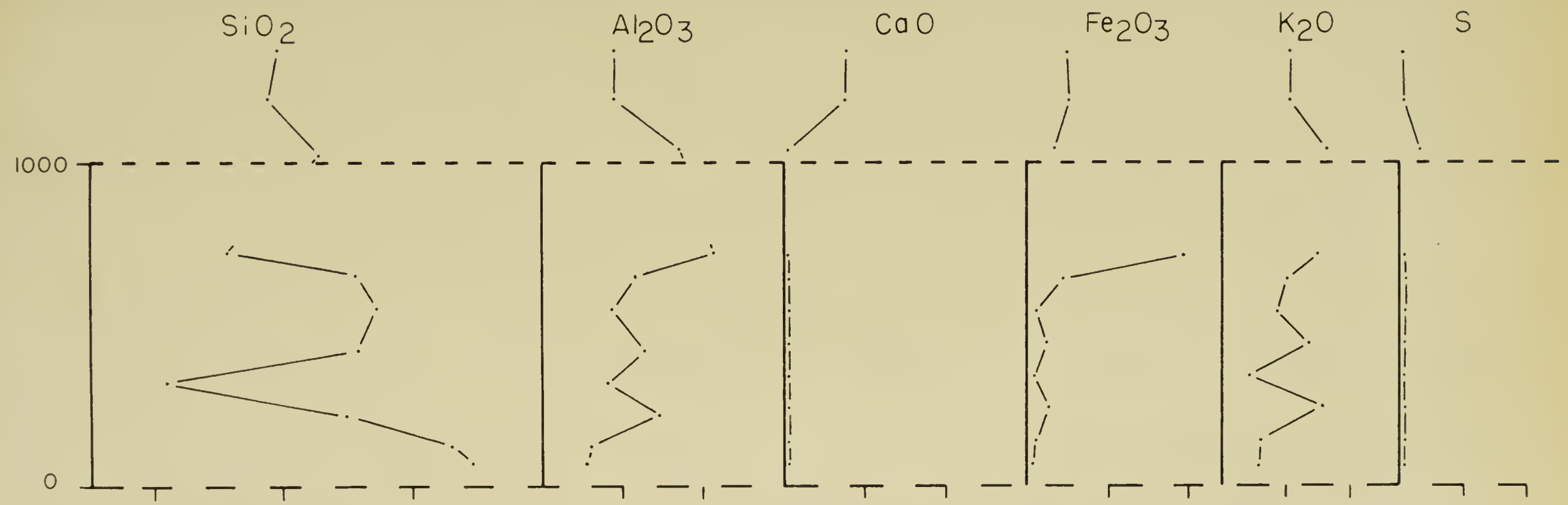
9 - Toad River : Major oxides

FIGURE 28

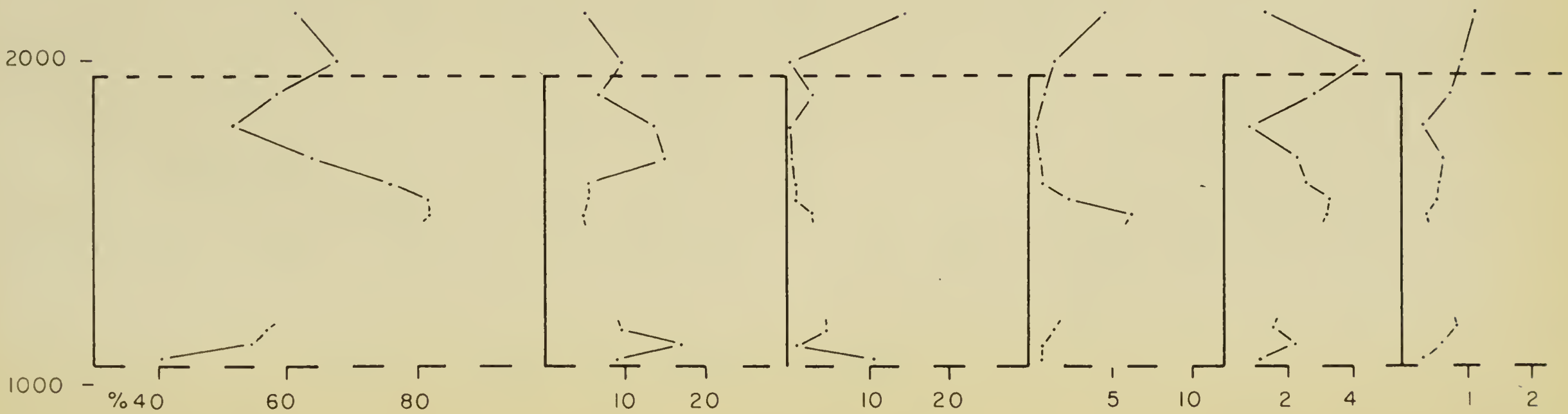


10 - 25BR64 : Major oxides

FIGURE 29

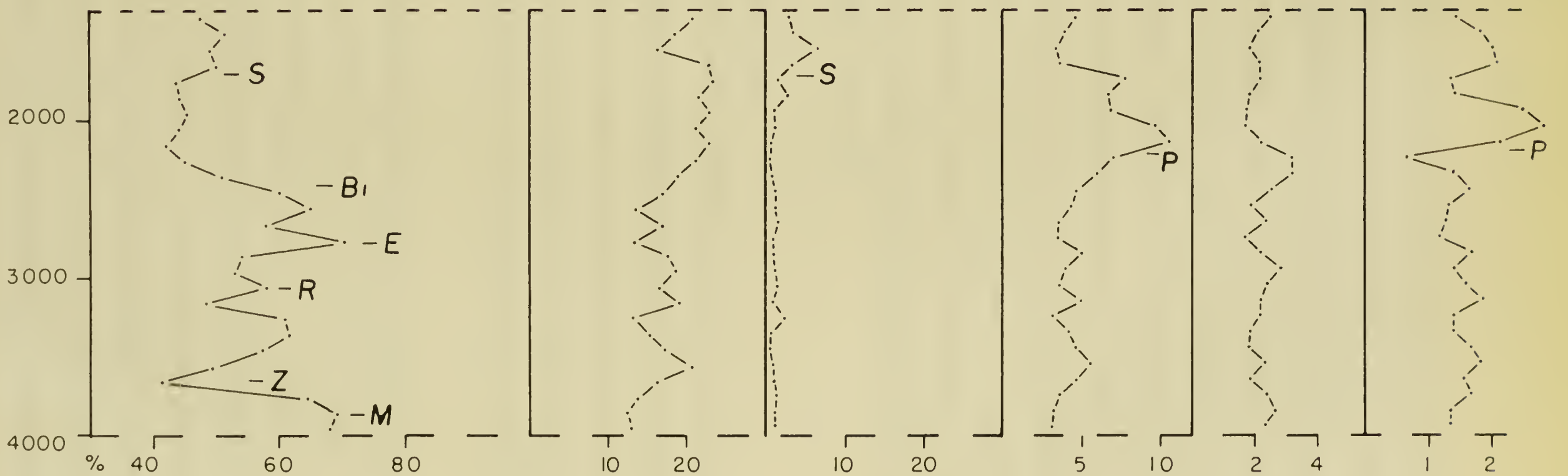


12 - P1-63 : Major oxides



11 - P 3 -63 : Major oxides

FIGURE 30



13 - E. Grayling : Major oxides

FIGURE 31

which normally characterize them. Faced with a choice between the two types of logs however, there can be little doubt that the mineral logs would prove more useful for correlation purposes, despite the fact that they are probably less accurate. On the major oxide curves, for example, total Fe_2O_3 is of limited value for correlation purposes. Mineralogically, the total Fe_2O_3 is represented by the three mineral species siderite, chlorite and pyrite. Partitioning of the iron among these three mineral species is of major value for correlation purposes (cf. siderite unit in Figures 10, 11, 13). In addition to correlation value we may gain from this partitioning some insight into the nature of the depositional environment, for example low pH and Eh inferred from formation of siderite, or transition of chlorite to septechlorite which also appears to reflect low pH and Eh conditions judging by the common association with siderite or highly pyritic units.

C. Trace Elements and Element Ratios

The trace elements selected for determination have been those which are known to display a strong tendency for diadochic substitution for the major elements of the study. Although manganese is present in amounts greater than those generally regarded as trace quantities, it has been included in this category because of its strong diadochic tendencies and because, so far as determined, no manganese minerals occur in the shale.

The ratios between geochemically similar pairs of elements might be expected to provide a useful correlation tool. Any variations in supply of the two elements as a function of time should be readily apparent. In addition, variations in mineralogy which affect the degree of substitution might be anticipated. Considering all of the above, the trace elements Mn, Sr and Rb were determined and the ratios Mn/Fe, Sr/Ca and Rb/K were calculated for each sample. The ratio between the geochemically dissimilar pair K/Al was also computed to permit further evaluation of the previously noted increase of K_2O with geologic time, as contrasted to the

constancy of Al_2O_3 with time.

The habitat of manganese in the sedimentary environment is, on the basis of published data, enigmatic. Observation of the occurrence of manganese nodules in recent deep-sea environments (cf. Shipek, 1960) have focused attention on this habitat. The survey of crustal abundances by Turekian and Wedepohl (1961) also indicates a concentration of Mn in deep sea clays, with an average content of 6,700 p.p.m. as compared with 1,000 p.p.m. in deep sea calcareous oozes. For Phanerozoic sediments however, their data show the inverse relationship, with an average Mn content for shales of 850 p.p.m. and for limestones 1,100 p.p.m.

The most extensive study of manganese distribution in Phanerozoic rocks appears to be that by Ronov and Ermishkena (1959), which encompasses 1,100 composite samples representing some 26,000 individual samples of all ages and lithologies from the Russian Platform. To summarize as briefly as possible, these authors found that:

(a) Mn content varied as a function of time, with an overall decrease during the Paleozoic but with a sharp maximum during the Devonian.

(b) Mn was paragenetically related to iron in shales and sands, with the Mn/Fe ratio closely approximating the values of .011-.026 for igneous rocks. In limestones, however, the Mn/Fe ratio increased sharply indicating a preference of Mn for this lithofacies.

(c) Maximum Mn content occurred in "coastal" (near-shore ?) facies, with a gradual decrease towards lagoonal and continental facies and a more abrupt decrease towards the open sea pelagic facies.

(d) Two types of distribution occurred relative to the concentration of Mn in limestone:

  (1) that in which the Mn content was about twice that of the associated shales, and

  (2) that in which the Mn content is about half that of the associated shales.

The authors associate the former pattern with humid climatic conditions and the latter with arid conditions. This association is apparently made on the presence or absence of equivalent red beds.

Rankama and Sahama (1949) have pointed out that the most favourable conditions for nonreversible precipitation of manganese include oxidizing environments and the presence of small quantities of calcium carbonate, into which the manganous ion enters readily because of the small difference in ionic radius relative to Ca. They also point out the stability of manganous bicarbonate in solution in the presence of reducing humic acids. It would appear then that the expectation should be for a generally decreasing Mn content towards the pelagic environment, as in fact was observed by Ronov and Ermishkena. The Mn enrichment of modern pelagic clays may well be a relatively recent phenomenon due to an exceptional Mn fixation ability acquired by some pelagic organisms, perhaps combined with a high rate of dissolution of calcium carbonate in an environment devoid of humic material.

The very close diadochic relationship between Rb and K may be gauged from the small spread in their ratio as calculated from the data of Turekian and Wedepohl (1961), shown in Table VI.

Table VI. Rb/K Ratios in Various Lithologies. After Turekian and Wedepohl (1961)

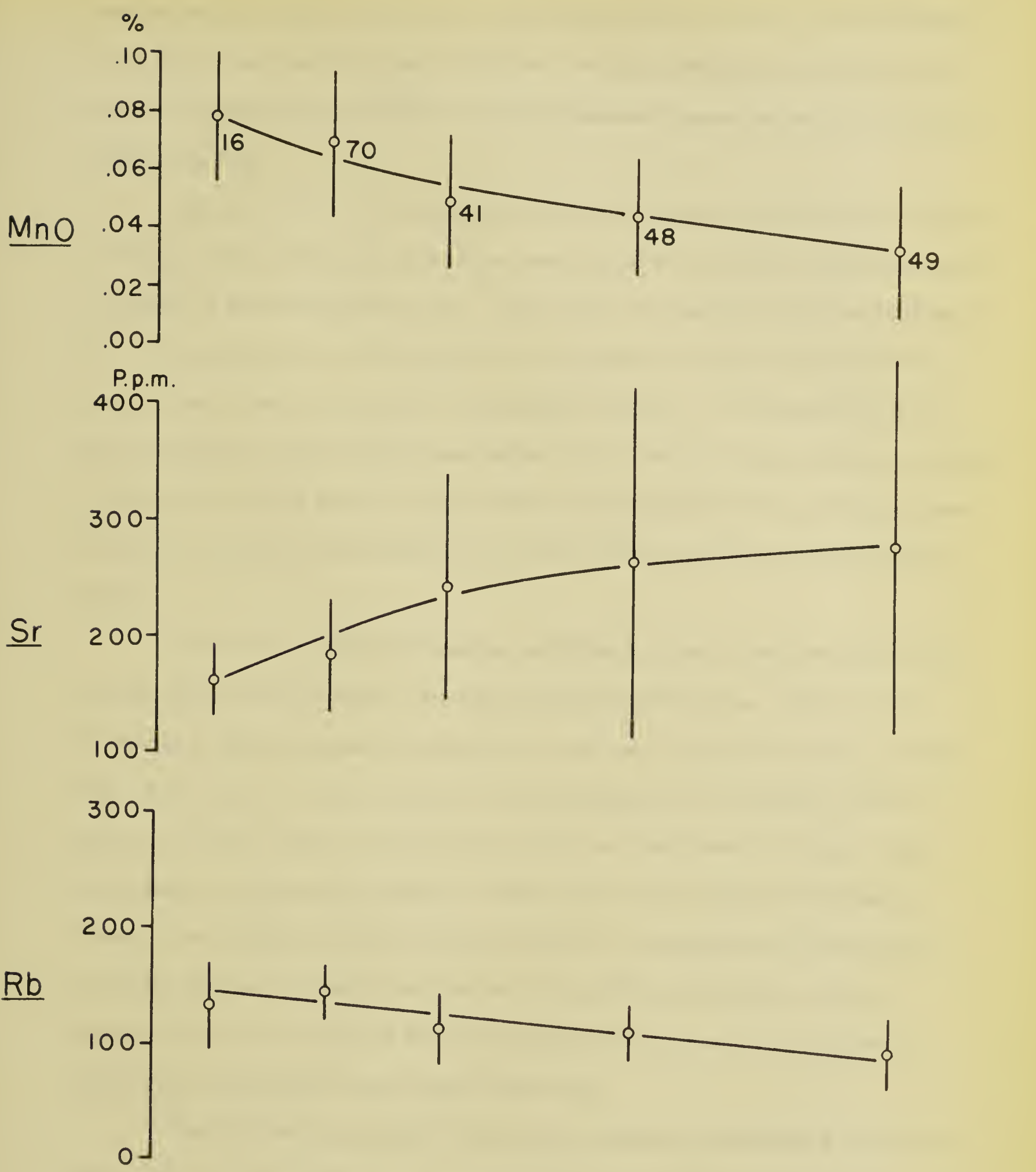
Basalts	Granites	Shales	Carbonates	Deep Sea Clays	Deep sea Carbonates
.0036	.004-.010	.006	.001	.0045	.0035

The close similarity of the ratio in the two different deep sea lithologies as compared with the spread as between shales and carbonates offers some reason to hope that this ratio might prove an effective water depth indicator. Further support for this possibility is obtained from the study by Campbell and Williams (1965) which shows a ratio

of .003 for continental beds, .004 to .005 for brackish and near-shore marine facies and .0068 for open marine facies. In the present study the Rb/K ratio varies from a low of .002 to a high of about .008. The vast majority of the values fall near the higher figure, and the low values all occur in shales which are interbedded with limestones. This tends to confirm the enrichment of K in the highly calcareous environment as suggested by the data of Turekian and Wedepohl.

The distribution of Sr in sediments is, as Turekian and Kulp (1956) have pointed out, governed by two rather opposed factors. One of these factors is the preferential absorption of Sr relative to Ca in the lattice structure of clays, the other is the diadochic substitution of Sr for Ca in carbonate minerals. The interplay of these two factors is such that Sr increases in amount with increasing calcite content, but the Sr/Ca ratio of shales poor in calcite is very high compared to that of calcitic shales. Since Sr substitutes much more freely in aragonite than in calcite, and since there has been strong evolutionary tendency in favour of development of aragonite-secreting organisms, this is one element for which we might expect to find a time dependency in the geologic record.

The time dependency in the distribution of the three trace elements of this study is examined in Figure 32. The decrease of MnO with increasing time is quite pronounced, and has the same direction and approximate magnitude as that observed by Ronov and Ermishkina (ibid) for the shales of the Russian platform. The fairly pronounced increase in average Sr content with time is accompanied by a large parallel increase in standard deviation. Such a result is precisely what would be anticipated if the increase in Sr were brought about by an organism or group of organisms which possessed a high degree of preference for a particular facies within the basin. The tendency here is opposed to that indicated by Turekian and Kulp (ibid) for Devonian and Mississippian shales. Their Mississippian average was, however, based on only seven samples, and in view of the large standard deviation for the Mississippian shales such disagreement is not surprising. The indication of



Trace Elements Vs. Time

FIGURE 32

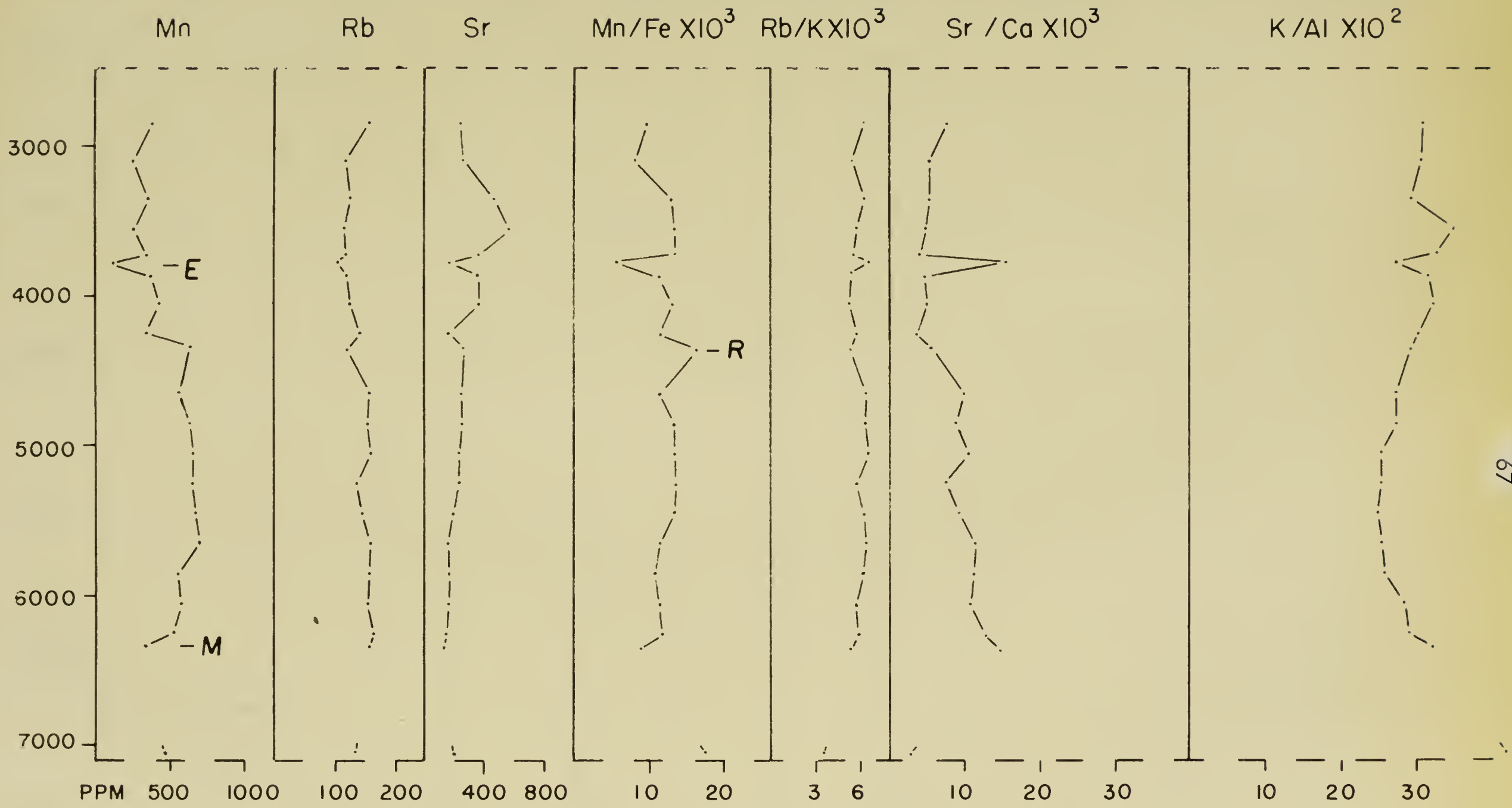
time dependency of Rb is slight, and very similar to that previously observed for K. Again it will be noted that there is sufficient overlap of standard deviations in all cases to indicate little possibility of a given elemental concentration characterizing a particular unit.

Again, as with the mineralogical and major element variations, the changes in trace element content and ratios have been plotted as a function of depth to permit assessment of their correlation value. These plots are presented in Figures 33 through 44. For control points which are fairly close together (cf. Figures 33 and 34) the copy of the curves is quite good. Over greater distances, (cf. Figures 33 and 35) the correlations would be highly speculative in the absence of other evidence, although on the other hand the data do provide some valuable confirmation for previous correlations, for example in the generally low level of all trace elements in the Exshaw Shale.

Some of the regional tendencies exhibited by these curves have substantial paleogeographic significance in the light of previous discussions. Thus it will be noted that total Sr decreases to the northwest and west (see Fig. 33 vs. Fig. 37 and Fig. 38 vs. Fig. 41). Total calcium is also decreasing in this direction, and at a faster rate so that locally very high Sr/Ca ratios are developed to the west, ratios which begin to approach the value of .0062 which is calculated from the data of Turekian and Wedepohl (1961) for deep sea clays. A comparison of the same pairs of figures referred to above shows that Mn also exhibits a significant westward decrease which, in the light of the Russian platform data, would be interpreted as reflecting a more pelagic environment to the west.

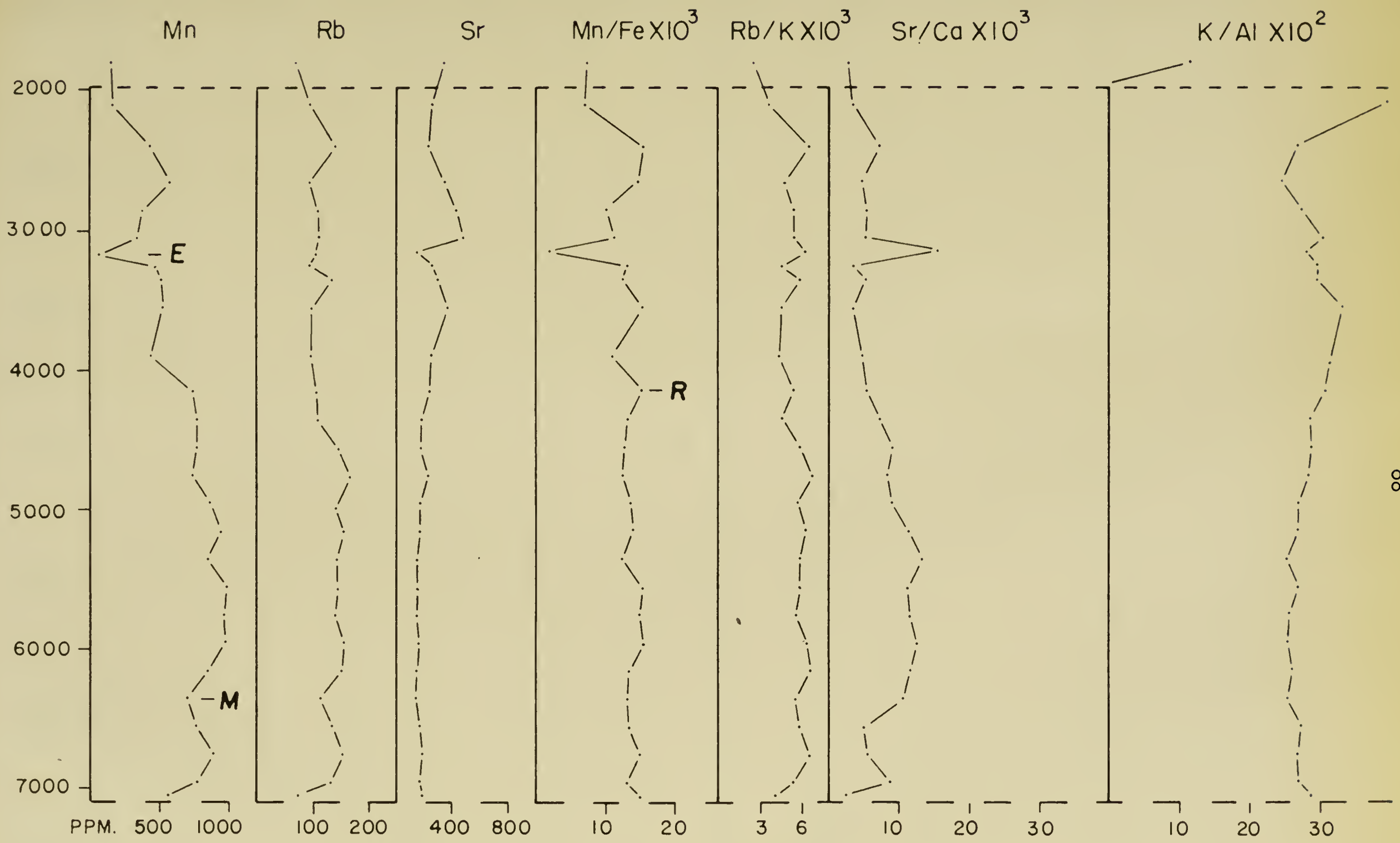
The K/Al ratio curve fails to show any consistent variation as a function of time. In most control points some tendency for an upward decrease of K_2O is evident in the lower portions, and in Figures 36 and 37 for example this is quite marked. In general however, and particularly in the more easterly control points, this tendency is overtaken in the upper portion by an increase in K/Al ratio in the

more calcareous intervals. In control points where shales occur which are interbedded with limestone, as for example the uppermost analyses of Figures 38 and 39, the K/Al ratio becomes very high. This behaviour would appear to reflect and confirm the well known preponderance of illite in carbonate-associated shales.



1- Clarke Lake c – 94 – L : Trace elements & ratios

FIGURE 33



2- Snake River A-1: Trace elements & ratios

FIGURE 34

3000
4000
5000
6000
7000
8000
9000
E
R
M
PPM 500 1000 100 200 400 800 10 20 3 6 10 20 30 10 20 30

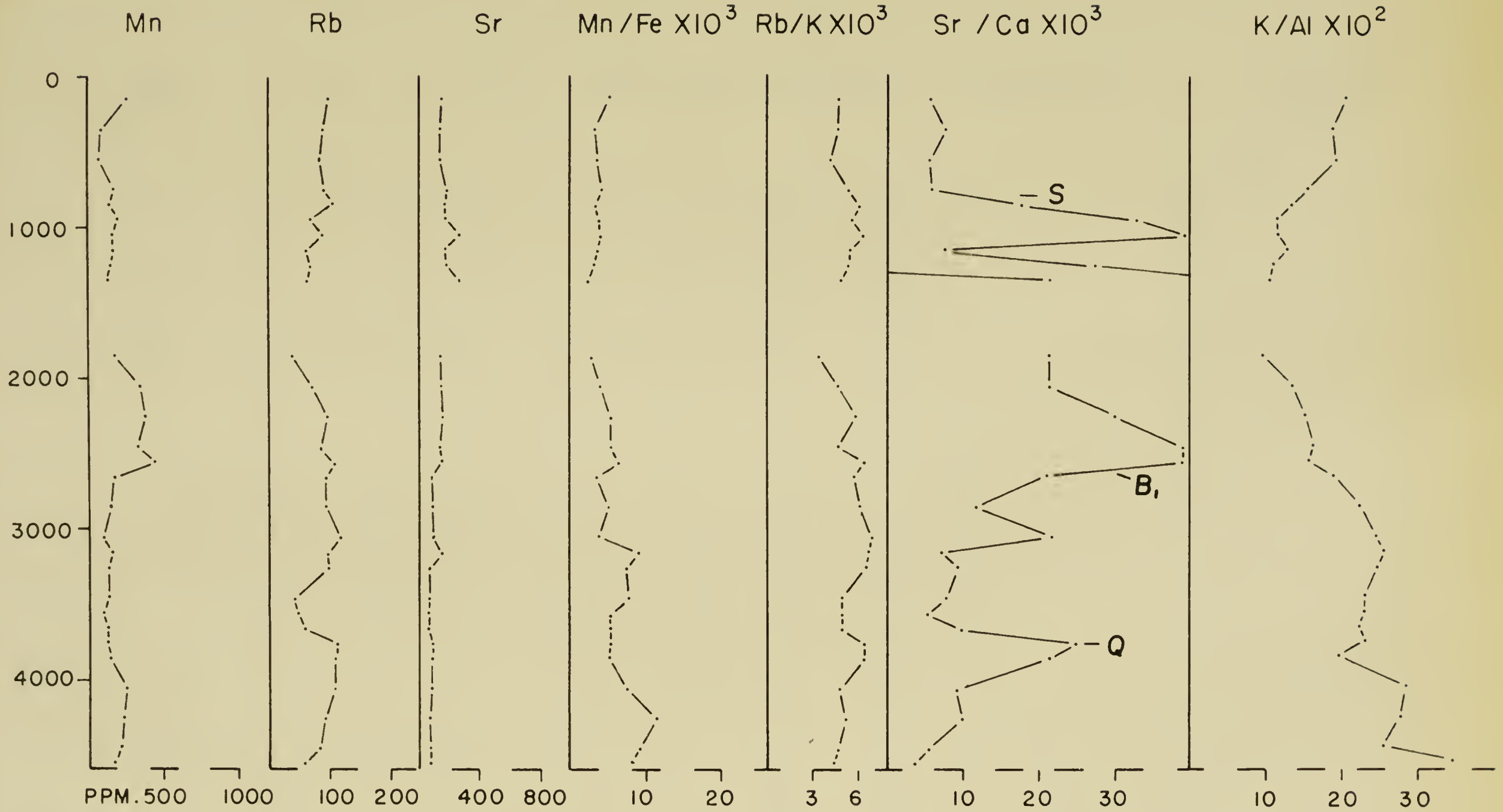
3- Deer Lake A-1 : Trace elements & ratios

FIGURE 35

5000
6000
7000
8000
9000
10,000
11,000
E
S
PPM 500 1000 100 200 400 800 10 20 3 6 10 20 30 10 20 30
70

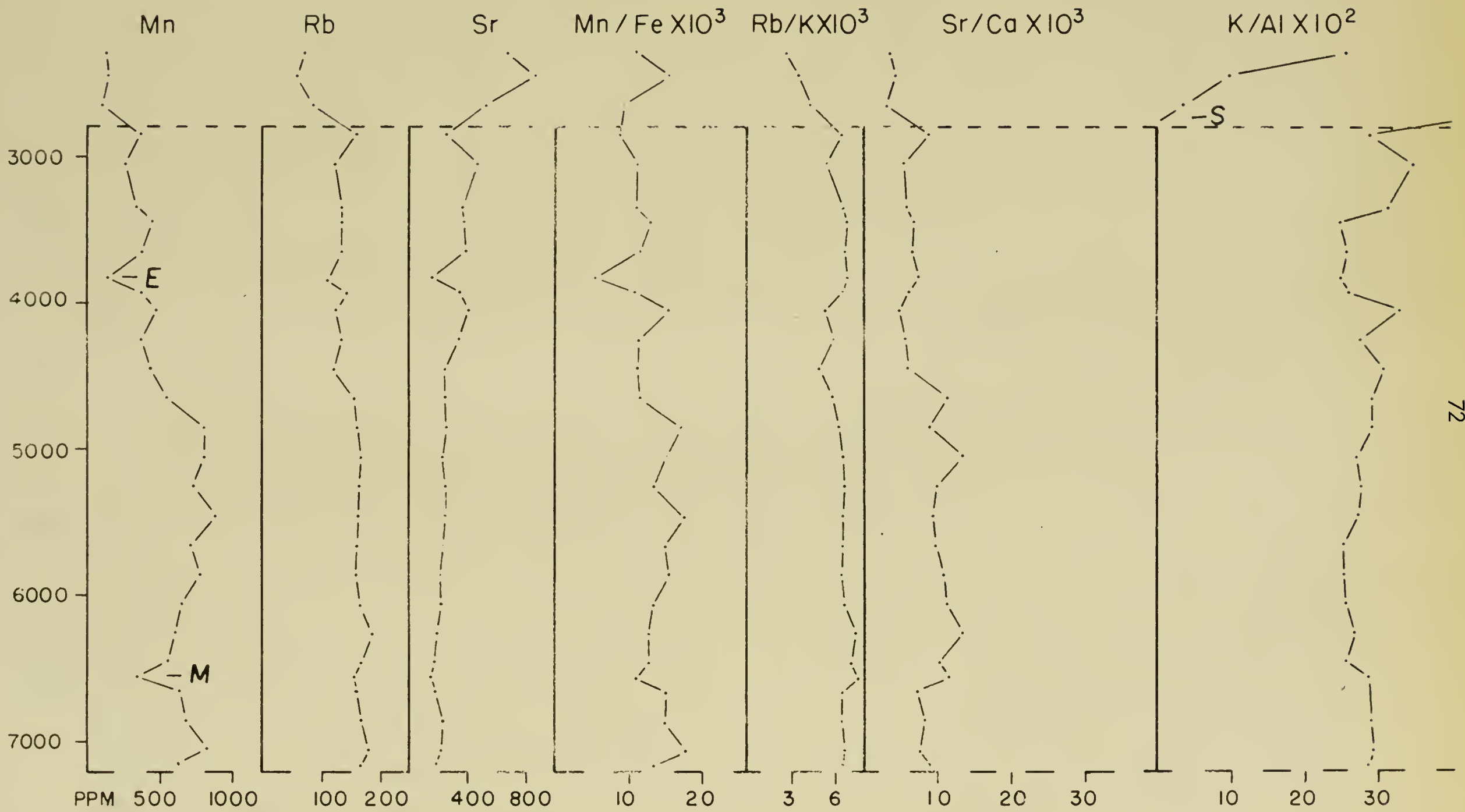
4 - Beaver River A-1 : Trace element & ratios

FIGURE 36



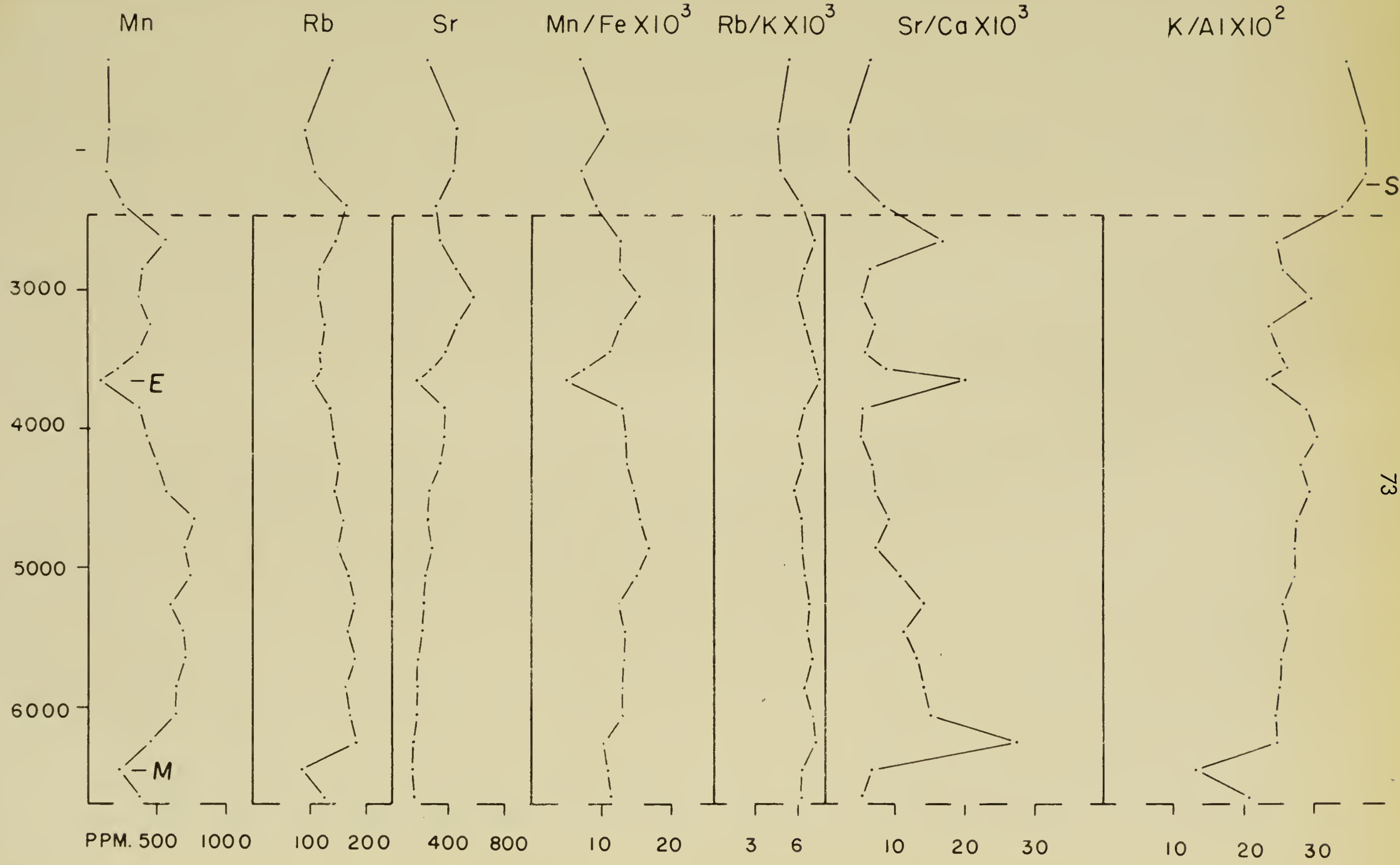
5- Beavercrow : Trace elements & ratios

FIGURE 37



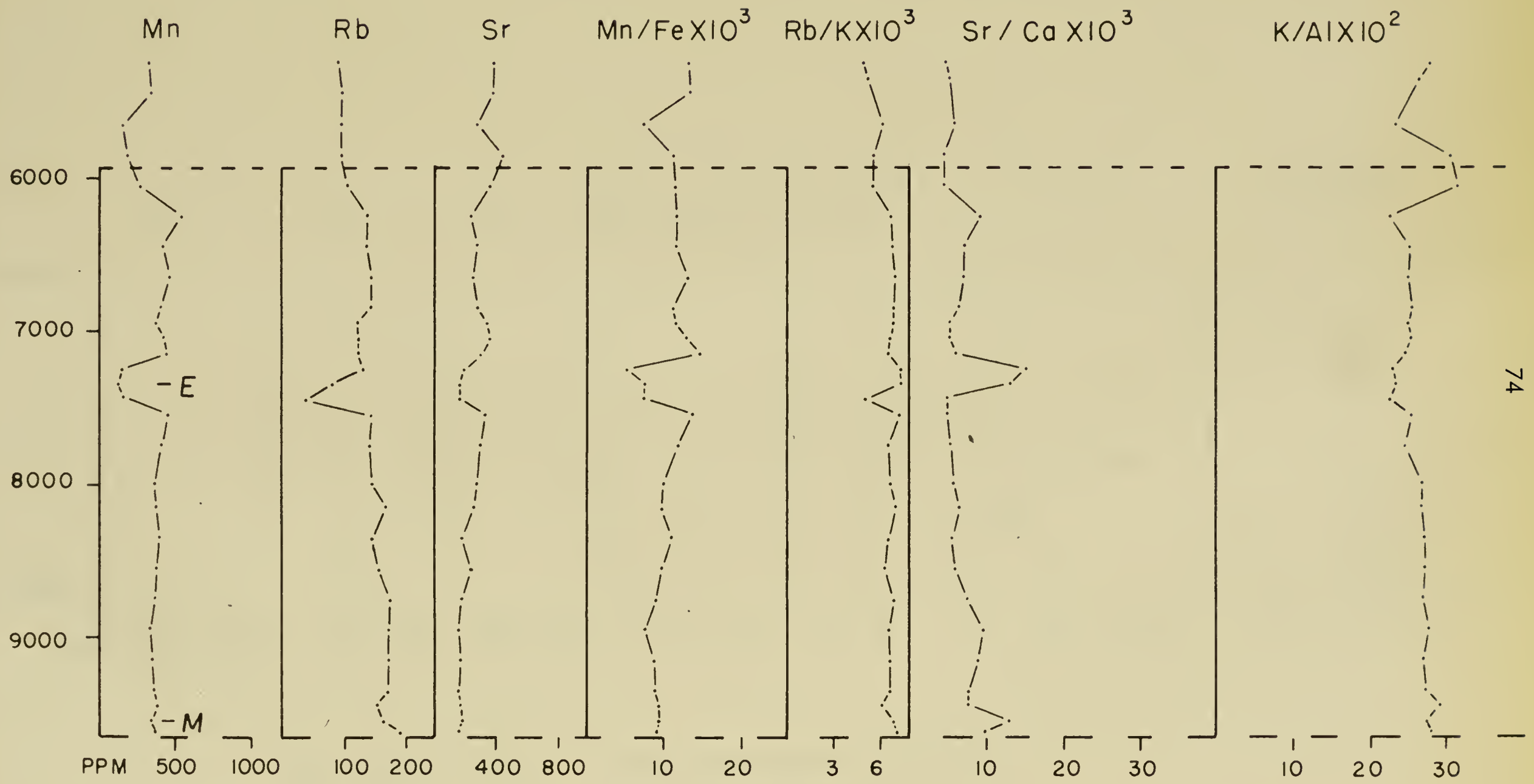
6 - Ft. Nelson # 2 : Trace elements & ratios

FIGURE 38



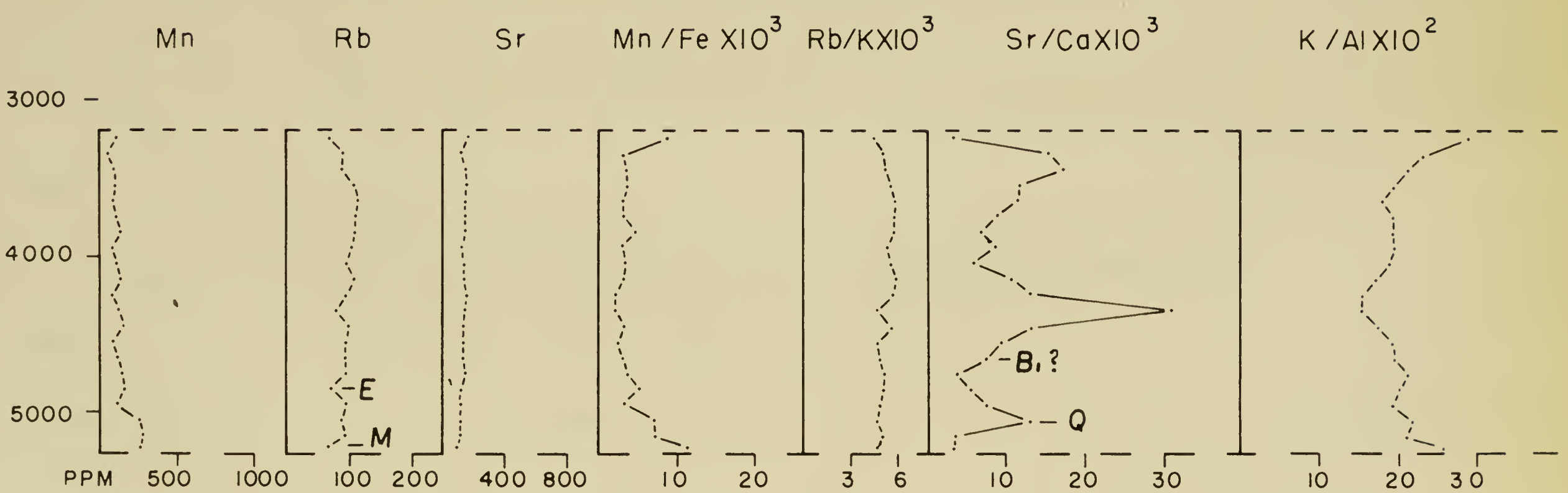
7- Evie Lake #1 : Trace elements & ratios

FIGURE 39



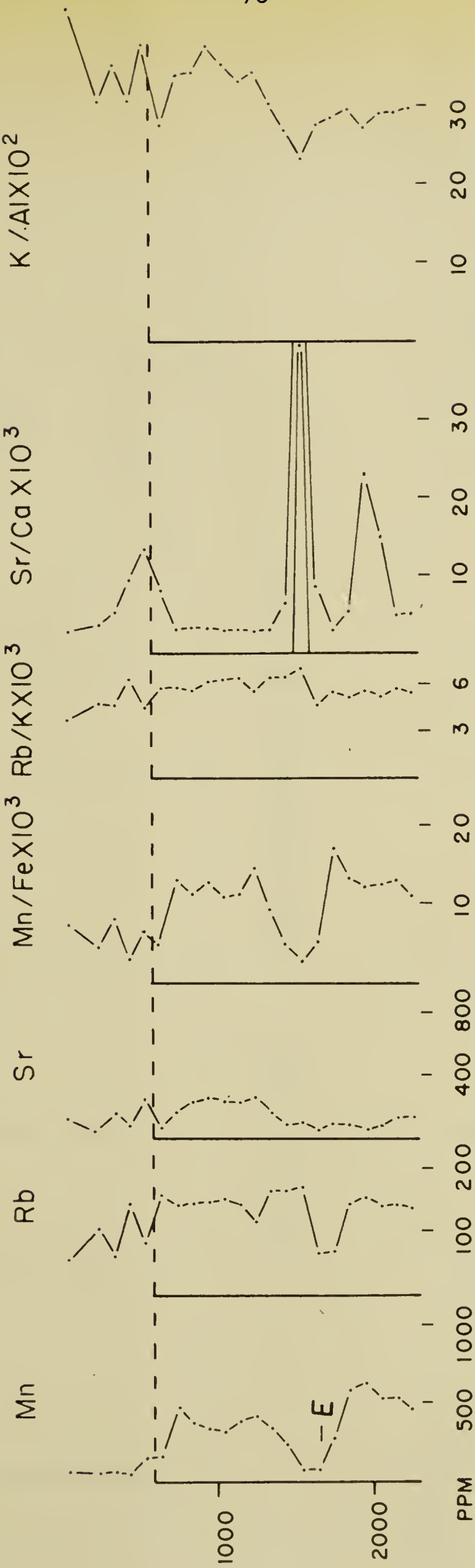
8 - Kledo : Trace elements & ratios

FIGURE 40



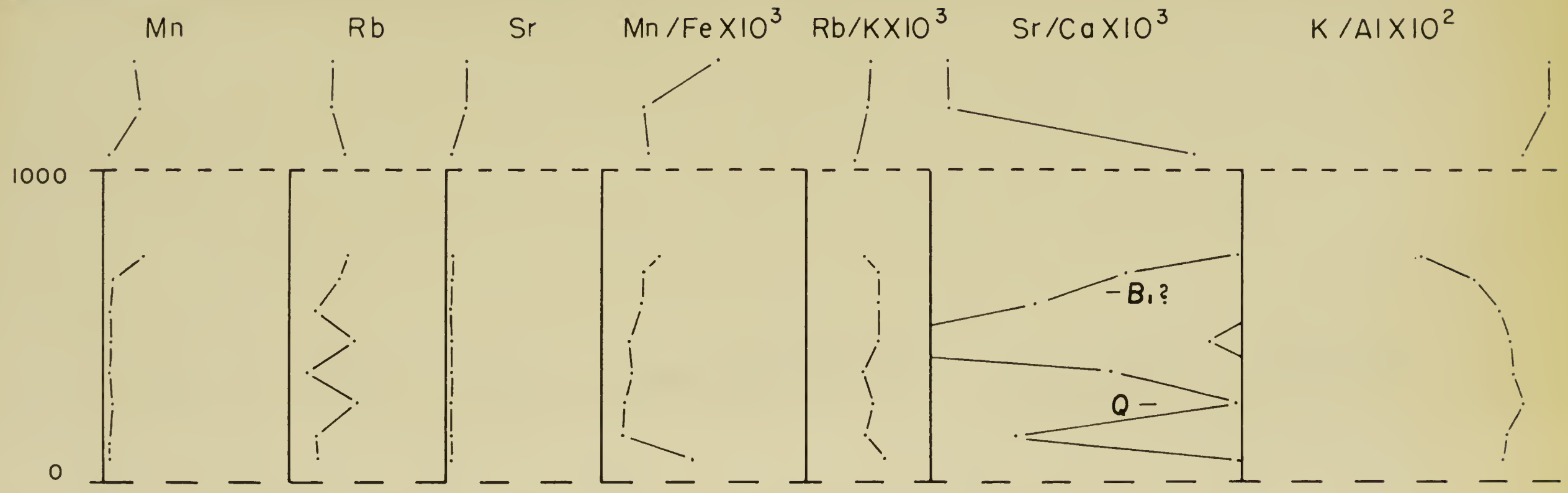
9 - Toad River : Trace elements & ratios

FIGURE 41

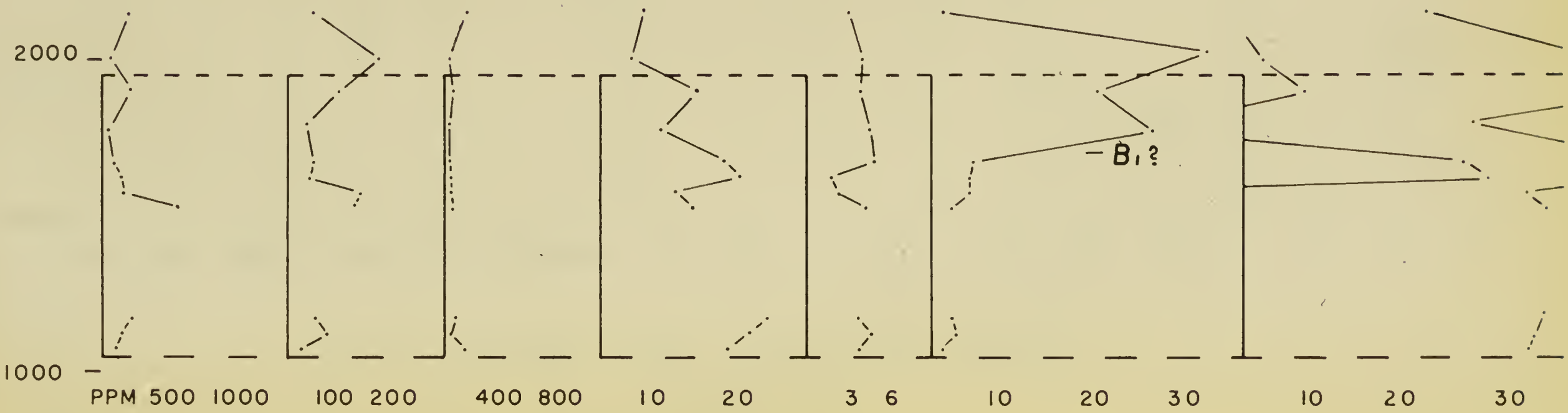


IO-25 BR64 Trace elements & ratios

FIGURE 42

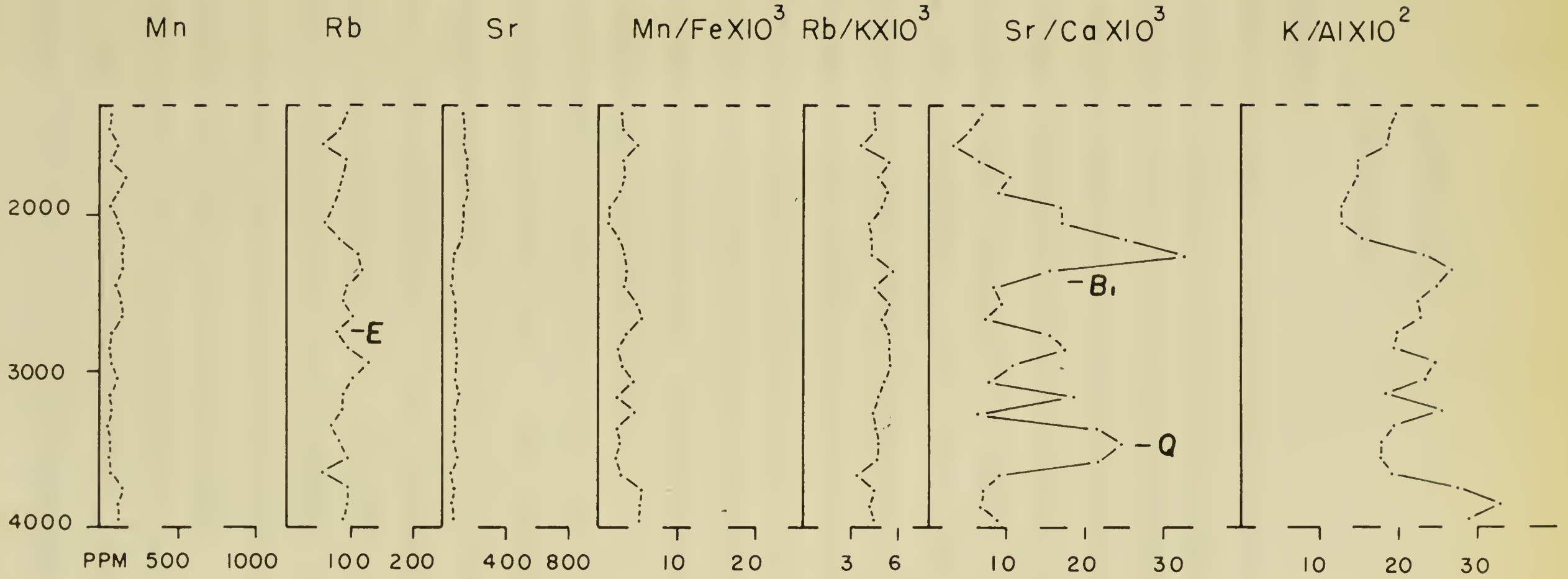


12-P1-63 Trace elements & ratios



11-P3-63 Trace elements & ratios

FIGURE 43



13 - E . Grayling : Trace elements & ratios

FIGURE 44

CHAPTER FOUR

STRATIGRAPHY

A. Faunal and Floral Elements

Before proceeding to an integration of the mineralogical and geochemical correlations we shall consider the limited paleontological and palynological evidence, which has some value for both correlation and paleoecological considerations.

Among the control points of this study two ammonoid occurrences are known to the writer. One of these is a small goniatite discovered in the drill cuttings of the Pan American Beaver River b-63-K well (control point #4) at a depth of 4,980 ft. i.e. some 950 ft. below the base of the Mattson formation. This specimen was identified by W. H. Ramsbottom (fide House, personal communication) as Cluthoris sp. This genus has been reported by Currie (1954) from the mid-Visean of Scotland, where it appears to be particularly abundant in a zone some 1200 ft. below the base of the Millstone Grit. This occurrence suggests that the sandy shales from 4,070 to 4,970 ft. in the Beaver River well are the lateral equivalents of the Debolt Formation and the correlative of the upper part of the Etanda Formation.

Sellers and Furnish (1960) have reported the occurrence of the new species Prolecanites warreni in the Toad River #1 well (control point #9) at a depth of 4,455 ft. This occurrence suggests a Mississippian age, but otherwise the new species is of limited correlation value. Sellers and Furnish infer an Upper Mississippian assignment on the basis of evolutionary trends, but this appears rather implausible on the basis of position of the specimen only 820 ft. above pre-Givetian carbonates. Geochemical correlations of this study show the occurrence to lie immediately above marker "P", i.e. at approximate Pekisko or low Osagean position in the succession.

Positioning of the Lower Mississippian/Upper Mississippian boundary within the study area is critical, since the correlations of Gray and Kasube (1963) of Debolt and Shunda-Pekisko in the Fort Nelson area are long range and apparently based entirely

on lithology. Evidence concerning the boundary between the two series was obtained in the B.A. - Pan American Klenteh c-15-I well, lying some four miles south of control point #3. Ostracods from the interval 2,700 - 2,760 ft. were identified by Dr. R. Green of the Alberta Research Council as Orthobairdia sp. and Bairdia sp., indicative of Rundle equivalence. In the interval 3,000 - 3,100 ft. Waylandella punctata Green, Libumella sp. cf. L. athabascensis Green, and Rectobairdia sp. aff. R. fragosa Morey are indicative of Shunda position. In the same well the present author has identified at 2,000 - 2,200 ft. the spores Murospora aurita, Anulatisporites sp., Triquitrites sp., Densosporites sp. and Reticulatisporites sp., an assemblage consistent with the Visean Murospora aurita assemblage of Playford (1962, 1963). At 3,000 - 3,100 ft. in the same well, Lophozonotriletes rarituberculatus, Velosporites echinatus and other less diagnostic forms belonging to the Lophozonotriletes rarituberculatus assemblage of Tournaisian Age were found. Thus the position of the Tournaisian/Visean boundary may, on both lines of evidence, be taken at the base of the massive carbonate section at about 2,800 ft. Lithologic and log correlations to the nearby Pan American Deer Lake well (control point #3) place this boundary at 2,480 ft. some 20 ft. below mineralogical marker "S".

Another ostracod occurrence of interest is that of Acratia similaris Morey and Cryptobairdia sp. aff. C. compacta Geis at 7,000 - 7,100 ft. in the Phillips-S R.-West Cdn. Kledo c-14-G well (control point #8), indicative, according to Dr. Green, of lower Banff. This occurrence lies 300 ft. above marker "E", which is located within the Exshaw Shale. The assumption that the Exshaw Shale of this area lies close to the Mississippian/Devonian boundary therefore appears justified.

No information was obtained in this study concerning position of the Upper Devonian/Givetian boundary. For purposes of this report the boundary is taken to lie at the position of the radioactive Muskwa shale member of the Horn River Formation. The Muskwa Member overlies the Slave Point Formation and therefore is above the

known uppermost limit of the genus Stringocephalus. By this criterion the assumed boundary may lie a short distance within the Upper Devonian.

No paleoecological significance other than marine origin can be attached to the above mentioned faunas. Of greater interest however are the siliceous sponge spicules illustrated in Chapter Two. De Laubenfels (1957) has stated:

"The Hyalospongea live only in deep water. Occurrence at less than 100 meters seems to be restricted to localities underneath permanent thick ice, in Antarctica. Their greatest abundance is at depths of 1,000 to 10,000 meters".

Although extrapolation of this observation to ancient conditions involves some risk, it would seem a reasonable assumption that the great abundance of sponge spicules in some of the shales of this area is indicative of relatively deep water conditions.

B. Correlation and Stratigraphic Interpretation

Figures 2, 3 and 4 of Chapter One, it will be recalled, assembled the control points of this study into three interlocking stratigraphic cross sections and indicated the extent of conventional correlations. These three figures are here repeated as Figures 45, 46 and 47 with the addition of the mineralogical and geochemical correlations suggested in Chapters One and Two. On these figures the solid lines represent the conventional correlations, lines with long dashes primarily mineralogical correlations, and lines with short dashes primarily geochemical correlations.

Correlation lines "S", "E" and "M" corresponding to top of Shunda Formation, basal Exshaw Formation and mid-Muskwa Member, have been indicated on the figures as somewhat heavier lines. These primary correlations serve to divide the Besa River Shale and equivalents into approximately Upper Mississippian, Lower Mississippian, and Upper Devonian Series and the Givetian Stage. The qualification "approximately" deserves emphasis at this point. Markers "S" and "M" may not correspond exactly to Upper/Lower Mississippian and to Upper Devonian/Givetian boundaries, and "E" is not precisely located relative to the Lower Mississippian/Upper Devonian boundary. Also, the designation "Upper Mississippian" does not include the Chesterian portion

#5 #4 #3 #2 #1

FANTASQUE

MATTSON

BESA RIVER FORMATION

"LOWER ELK POINT GROUP"

S P E K R Y Z M

DEBOLT

SHUNDA-PEKISKO

BANFF

Exshaw

Kotcho

Tetcho

Trout River

Kakisa

Redknife

FORT SIMPSON

Muskwa

HORN RIVER

KEG RIVER

Slave Pt.-Presqu'ile

Chert

Limestone

Inb'd Ls. & Sh.

Dolomite

Shale

Siltstn; intb'd Ss. & Sh.

Sandstone; Quartzite

0 5 10

MILES

0 1000ft. 1

FIGURE 45

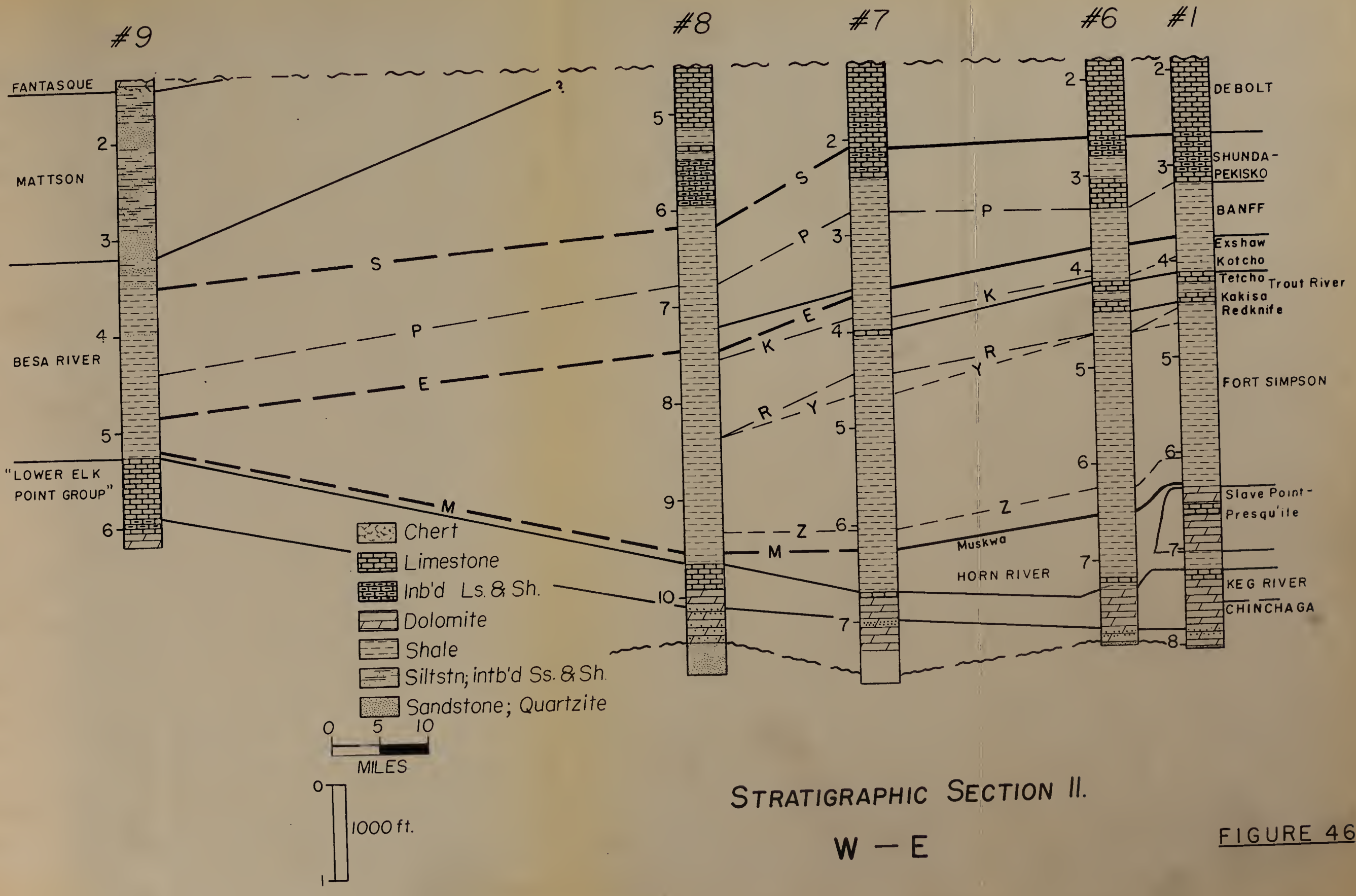
STRATIGRAPHIC SECTION I.

NW – SE

of the Mattson formation. These approximations should be borne in mind in the ensuing discussion.

Figure 45 shows that the Givetian shales thin consistently northwestward from the Fort Nelson area. The exact position of marker "M" in control points #4 and #5 is debatable; in control point #5 for example the last 100 ft. composite sample shows Muskwa characteristics, but these are rather subdued. It is concluded that the Muskwa lies within this interval, but exactly where is not determinable. The Upper Devonian Series thickens northwestward from Fort Nelson to control point #3, the begins to thin. The thinning is initially most marked in the basal portion, as indicated by markers "R" and "Y". The Lower Mississippian Series reaches maximum thickness in control point #4, then thins to control point #5. It would seem highly probable that the thick sandstone unit to which marker "P" is correlated in control point #5 is the Yohin Formation of Harker (1963), with the overlying sands and shales representing his Etanda Formation. The Yohin and Etanda sandstones are herein interpreted as deep water turbidites since they are enclosed by black pyritic and sideritic shales which show no suggestion, either lithological, mineralogical or geochemical, of shallow water origin. The Upper Mississippian Series shows maximum thickness at control point #3; west of this point it undergoes a facies change from shelf carbonates of the Debolt Formation to shales and minor sandstones equivalent to the upper part of the Etanda Formation.

Figure 46 shows a very similar pattern to that of Figure 45. The same pronounced westward thinning of the Givetian shales is evident. The Upper Devonian Series reaches maximum thickness in control point #7, then thins westward very rapidly. The Lower Mississippian Series is also at a maximum in control point #7, but westward thinning beyond this point is slight. In contrast, the Upper Mississippian reaches greatest development at control point #8, then changes facies from carbonate to shale and thins abruptly westward. Figure 46 shows some deviation among the



STRATIGRAPHIC SECTION II.

W — E

FIGURE 46

different types of correlations. Thus in control point #8, the black radioactive shale unit which is characteristic of the Exshaw Shale is abnormally thick. Mineralogical marker "E" occurs near the base of the overthickened Exshaw, suggesting that the upper part of that unit may be a local black shale phase of the lower Banff. Similarly, mineralogical marker "R" and geochemical marker "Y" show anomalous behaviour, sometimes coinciding and at other times diverging. The explanation would appear to lie in two distinctive marker units very close together so that at in one place they have both fallen within a single 100 ft. composite sample whereas in other places the boundary between consecutive 100 ft. composite samples lies between them.

Figure 47 shows that the condensation of the Besa River shale is most pronounced in the surface sections of control points #11 and #12. Unfortunately, correlation of these control points is also questionable, although those correlations which are indicated plus extrapolation of the westward thinning previously observed in Figure 46 do suggest that all of the shelf equivalents are probably represented in these extremely thin intervals. The Mattson Formation, it will be noted, is also very thin in these sections and thickens abruptly northward.

Having reviewed the correlations, it is now appropriate to consider possible interpretations for the observed westerly thinning of the Besa River Shale. Firstly, examination of the N-S stratigraphic section, Figure 47, suggests as an initial working hypothesis that the thinner sections represent a tectonically positive area, perhaps with periodic emergence and erosion and culminating in a final major uplift which shed the Mattson clastic wedge into an accompanying basin to the north. This appealingly simple hypothesis fails to stand the test of observed facts. Firstly, neither the Upper Mississippian nor the Givetian shelf carbonates show any sign of reappearance to the west as would be expected for shallow water conditions approaching a positive area. Secondly, the correlations suggest that all shelf units are represented by equivalents in the condensed sections, and no evidence of truncation of one marker by

#10 #11 #12 #9 #13 #5

PROPHET FM

BESA RIVER FM.

FANTASQUE FM.

MATTSON FM.

S

P?

P

B_1?

B_1

E?

E

M

Z

?

0 1 2 3 4 5 6

Chert
Limestone
Intb'd Ls. & Sh.
Dolomite
Shale
Siltstn; intb'd Ss. & Sh
Sandstone; Quartzite

0 5 10
MILES

1000 ft.

STRATIGRAPHIC SECTION III.
S—N

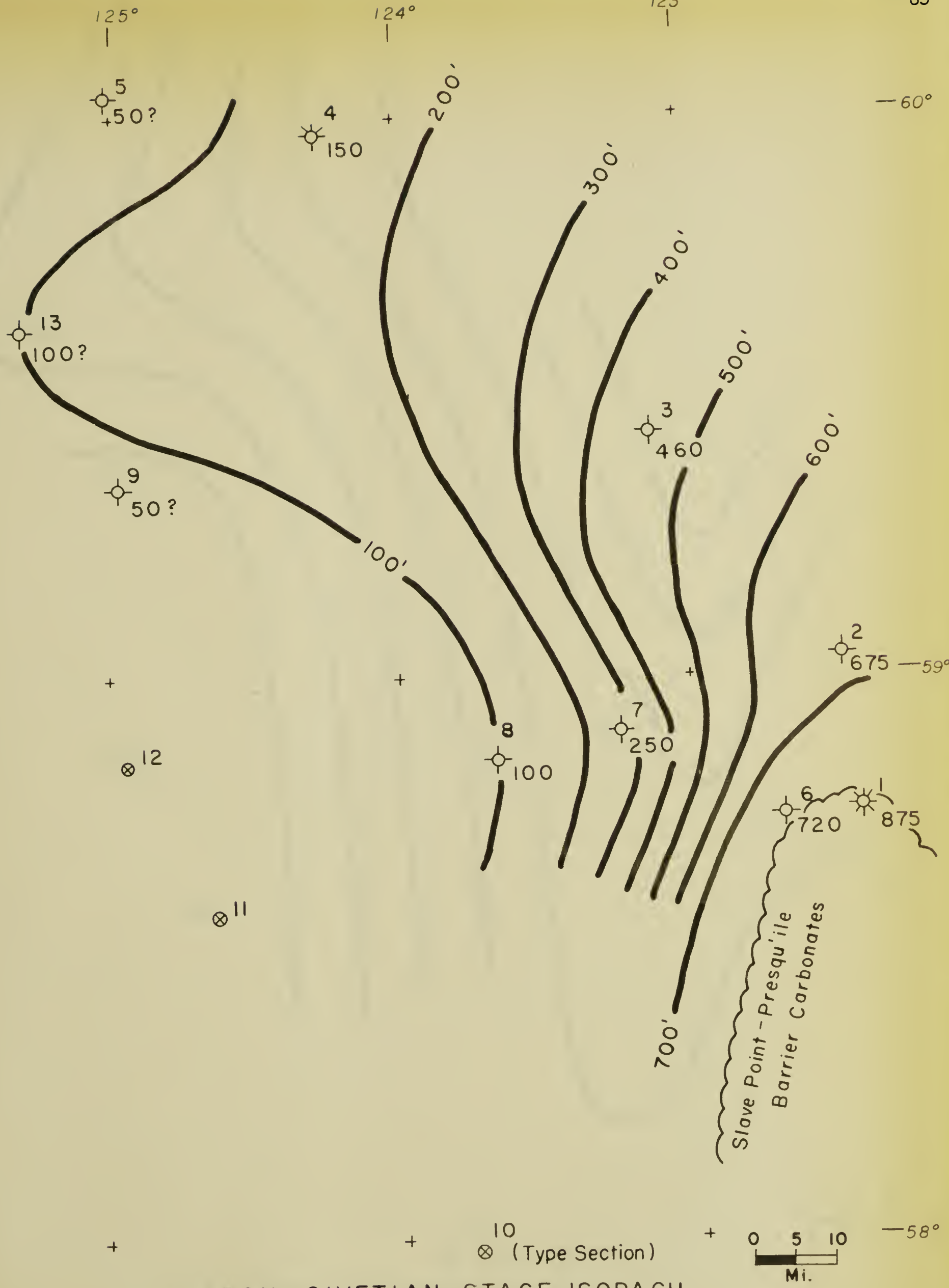
FIGURE 47

another is seen. Thirdly, it has been shown in Chapter Two that the Mattson clastics show minimum grain size to the south and coarsen towards the north, indicating that the source of the Mattson wedge lay to the north and not to the south. Finally, as we have seen, the Besa River shales contain siliceous sponge debris suggestive of a deep water origin.

The second working hypothesis meriting consideration is one of depositional slopes into a deep water environment. Rich (1951) has proposed a model of basin infilling in which he visualizes the process as one involving a succession of prograding wedges as opposed to the classic "layer cake" concept. Under the Rich hypothesis the condensed sections would represent the deep water fondothem, the thickest sections would mark the upper edge of the clinothem, and the somewhat thinner sections to the east of the depositional maximum would represent the undathem. This model of the process of basin infilling has received considerable support in subsequent stratigraphic studies. Thus Adams et al. (1951) showed that the late Pennsylvanian shelf carbonates of the Midland basin, which are over 3,000 ft. in thickness, are represented by less than 500 ft. of shaly limestone in the basin centre. Support for this view and additional details have been provided by Rall and Rall (1958) and by Van Siclen (1958). The latter author extends the same depositional model to the coastal plain sediments of the Gulf of Mexico. Other striking examples of the undathem-clinothem-fondothem model of basin fill have been provided by Jackson (1964) and, relative to the Ireton shale basin of central Alberta, by Oliver and Cowper (1963).

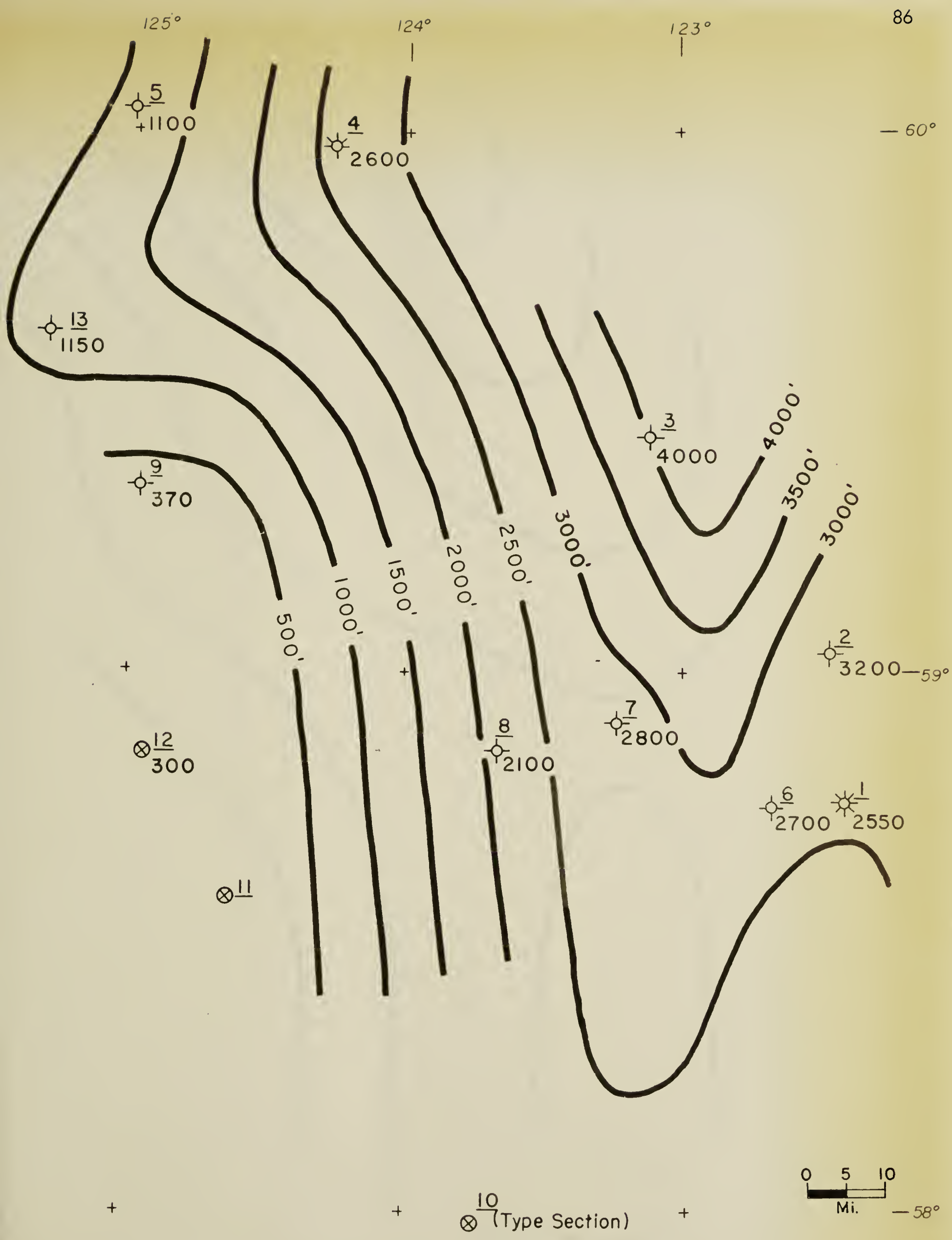
This hypothesis has immediate appeal in terms of the very objections which were raised to the previous one, namely association of deep water characterics with the condensed sections. In order to further evaluate applicability of the model, isopachs of the Givetian Stage and Upper Devonian, Lower Mississippian and Upper Mississippian Series have been constructed and are presented in Figures 48 through 51.

Figure 48 shows that the maximum thickness of Givetian shale, about 700



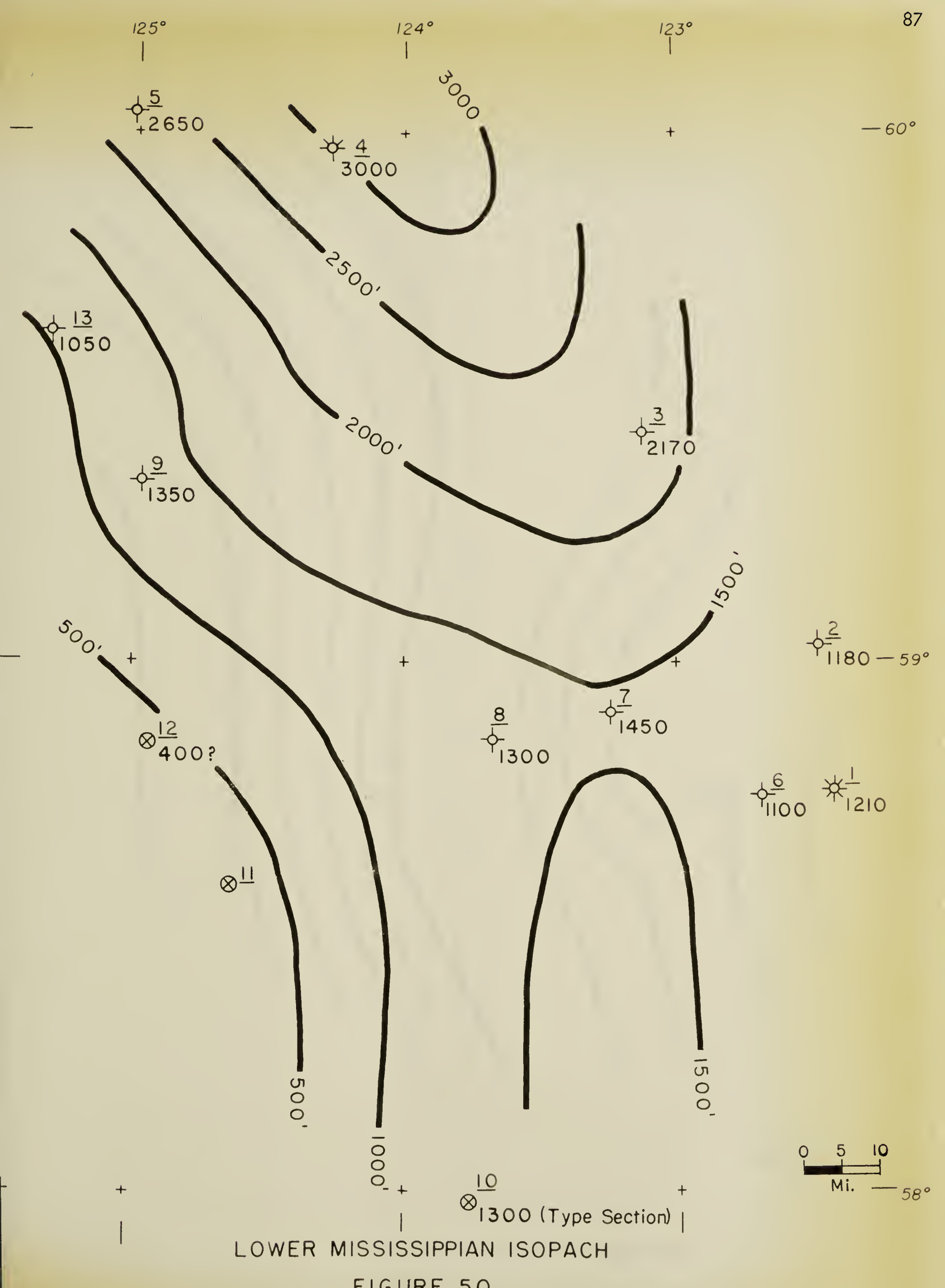
APPROX. GIVETIAN STAGE ISOPACH

FIGURE 48



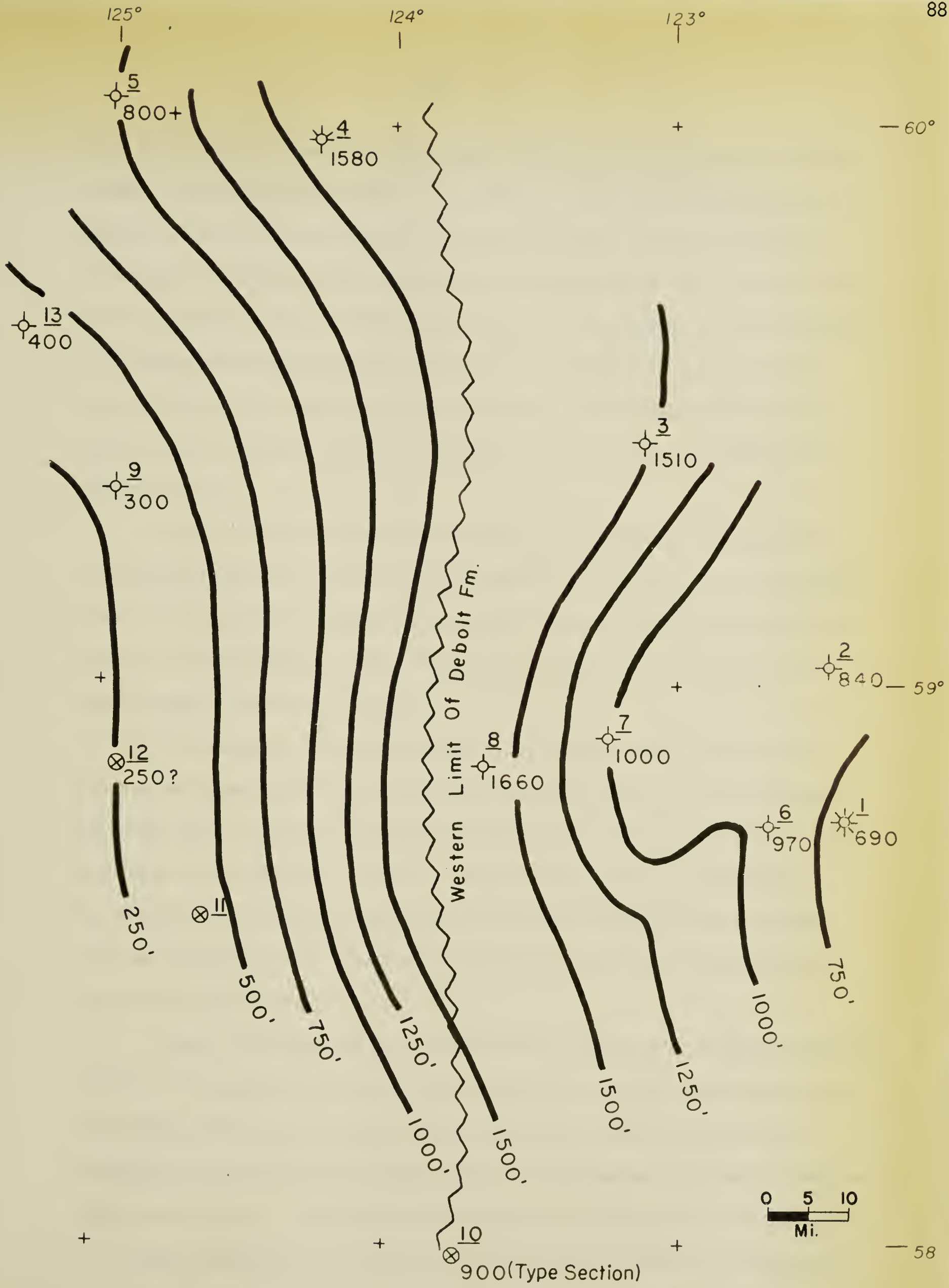
UPPER DEVONIAN ISOPACH

FIGURE 49



LOWER MISSISSIPPIAN ISOPACH

FIGURE 50



UPPER MISSISSIPPIAN ISOPACH

FIGURE 51

feet, is found at the immediate western edge of the Slave Point-Presqu'ile carbonate complex, which may be regarded as the undafacies. The clinoform slope drops off abruptly westward from the edge of the carbonate complex, resulting in Givetian shale isopachs of 200 ft. within some 25 miles. Beyond this the unit continues to thin, but at a much slower rate in the fondo environment. It is apparent that the isopach of the Givetian shales is controlled by the position of the edge of the economically important Slave Point-Presqu'ile barrier carbonates. In this connection the thick isopach value in control point #2 is of interest in terms of possible proximity to a carbonate front.

Figure 49 shows that the axis of maximum Upper Devonian deposition has shifted farther west, now lying on a line immediately east of control point #3 and #7. From this thick axis the clinoform slopes gradually westward and the clinothem thins at a rate of about 70 feet per mile. Fondothem thicknesses of less than 500 ft. are reached within a distance of 50 miles.

The process of westward progradation of the upper edge of the clinothem observed in Figures 48 and 49 is continued in Figure 50, where the axis of maximum Lower Mississippian sediment accumulation can be seen to have moved to a line lying to the west of control points #3 and #7. The fondo environment has undergone a similar westward shift, since control point #9 which contained a minimum or fondo thickness of Upper Devonian shales now contains an intermediate clino thickness of Lower Mississippian shales.

Figure 51 demonstrates that the undathemic carbonates of the Debolt Formation establish their westward limit at the top of the clinoform slope of the preceding Lower Mississippian. The locus of maximum Upper Mississippian deposition lies at and immediately in front of this facies edge, again showing westward progradation relative to the underlying unit. The clinoform slope appears to be steeper than that observed in the Lower Mississippian, and consequently the fondo environments of the two units

lie in about the same position. The limestones of the Prophet Formation, a lateral equivalent of the Debolt Limestone, are characterized by up to 50% bedded and nodular chert (cf. Hovdebo, 1962). The Prophet limestones are represented in this study only at control point #10. It is interesting to note that here they appear to extend onto the clinoform, and that they probably represent a somewhat deeper water clino facies of the Debolt.

The overall depositional slopes into the basin permit some estimate of water depths at various times. It can be assumed that the reefal margin of the Slave Point-Presqu'ile complex extended well into the zone of wave action and may even have emerged at low tide. Thus the ensuing Muskwa Member in the easterly control points can scarcely have been deposited in more than 100 - 200 ft. of water. Since the Givetian shales thin westward by an amount in the order of 650 ft., a depth of water of 750 - 800 ft. is indicated for the more westerly control points. This estimate ignores post-depositional compaction which would, if taken into account, increase the depth differential between the two areas.

Considering in similar vein the Upper Devonian, it seems probable that the Tetcho Limestone of control point #9 would have been deposited in the photic zone and that the overlying Kotcho Shale represents an only slightly increased depth. Thus a depth of 300 - 500 ft. might not be an unreasonable estimate for the water depth in the Fort Nelson area at the onset of Exshaw Shale deposition. At control point #9, however, the Exshaw was being deposited on a surface which lay deeper by the difference in isopach between the two points, which is about 2,200 ft. Thus the depth of water at point #9 at the onset of Exshaw deposition would have been in the order of 2,500 to 2,700 ft. Again the estimate is minimal, since post-depositional compaction would augment the figure and since no account has been taken of possible westward downwarping during Upper Devonian deposition, a possibility which must be regarded as very probable in view of the observed westward thickening of

the pre-Givetian carbonates.

Accepting the values of the Geological Society of London Phanerozoic time-scale (Quart. J. Geol. Soc. Lond., 1965, 120 S, pp. 260-262) of 14 million years for duration of the Upper Devonian, then the average rate of deposition indicated at control point #9 is 0.8 cm. per 1,000 years. This rate of deposition is only slightly greater than that of 0.5 cm. per year quoted by Ericson et al. (1961) for areas of slow continuous non-turbidity current deposition in recent Atlantic deep sea deposits.

It is pertinent to enquire at this point as to what became of the large unfilled basin which occupied the western part of the area at the close of Upper Mississippian time. In the northern part of the basin, the answer is immediately evident in the form of the Mattson clastic wedge, originating from some major uplift to the north and/or northwest and possibly being derived from the shallow marine to continental clastics of the Imperial formation of Upper Devonian Age. The supply of Mattson clastics was not, however, sufficient to fill this basin as evidenced by the thin equivalents in control points #9 and #12. Pelletier (1961), in his study of the Triassic deposits of this area, notes the occurrence of up to 6,000 ft. of marine Triassic beds in the vicinity of Racing River which lies only six miles west of control point #12. The basal part of this thick section consists of dark shales and siltstones of the Grayling Formation. It seems reasonable to suggest that this thick marine Triassic section constitutes the final basin fill of the southern part of the basin. If this is correct, then the central portion of the basin should contain sediments representing uninterrupted deposition from Middle Devonian to late Triassic time. The only clearly demonstrated evidence to the contrary known to the writer is the unconformity between Fantasque and Mattson Formations referred to by Harker (1963). Evidence for this unconformity lies north of the 60 th. parallel however, on the extreme northern and, on the evidence of the Mattson clastic wedge, tectonically active margin of the basin.

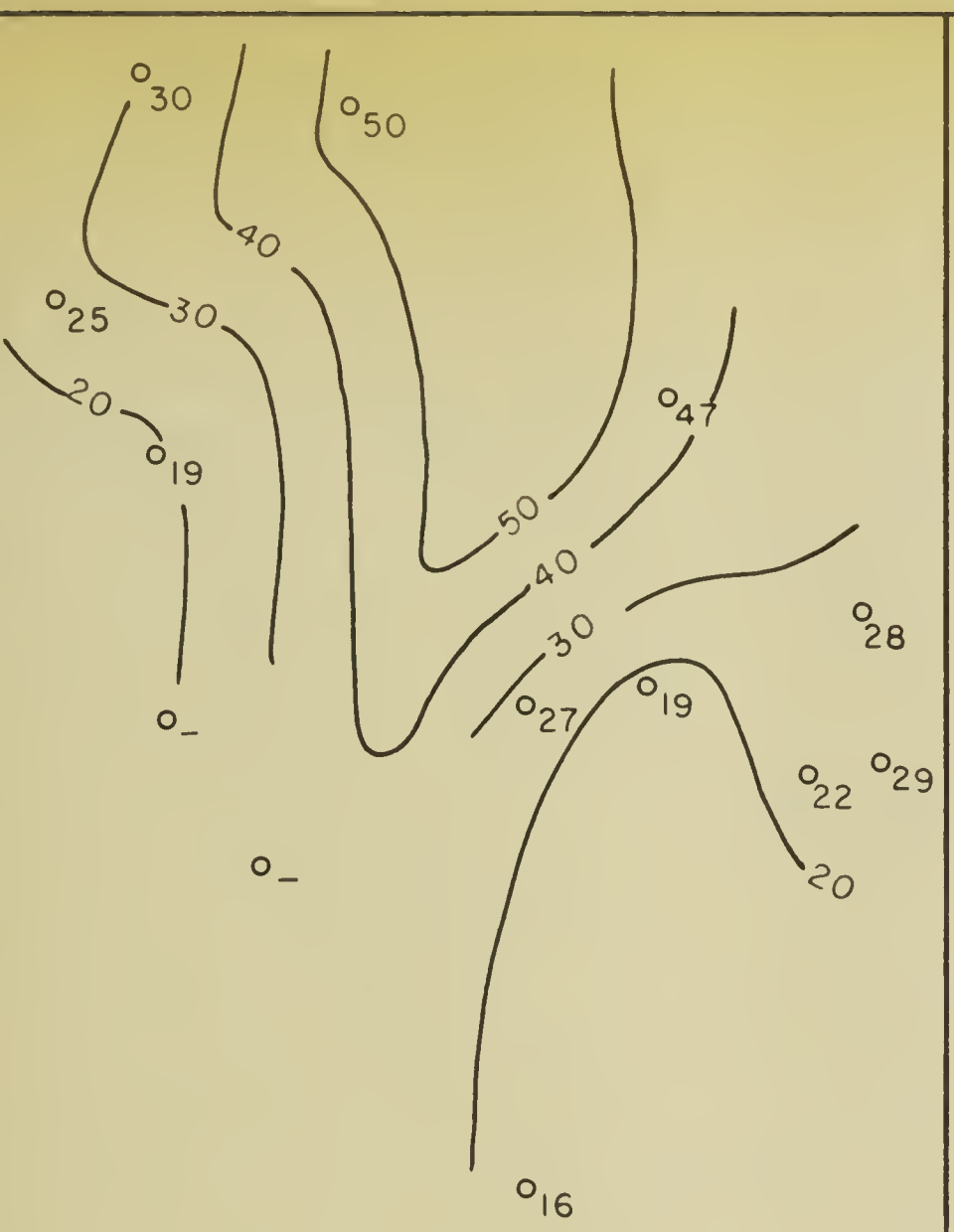
In personal discussions with geologists familiar with the study area, evidence

has sometimes been advanced for the existence of unconformities within the Besa River Shale and its lateral equivalents. While some of this evidence is debatable, some, including evidence of channeling along apparent erosion surfaces in well exposed surface sections, is rather convincing. It must be noted however that to oceanographers evidence of erosion on the present ocean floors is commonplace. Thus Ericson et al. (1961) indicate that about one in ten cores from the Atlantic show the occurrence of pre-Pleistocene deposits at the top of the core; rocks as old as Cretaceous are found exposed at depths of up to 3,900 meters. In the Pacific, Revelle et al. (1955) indicate exposure of mid-Tertiary clays on low hills at a depth of 5,000 meters. Turbidity currents, slumping and resulting mud flows are apparently the agents responsible for this deep-water erosional activity. Evidence of similar sub-aqueous erosion should be anticipated in the Besa River Shale in view of the rather steep depositional slopes. Such evidence does not constitute evidence for unconformity in the customary implication of that term as to uplift and exposure to sub-aerial erosion.

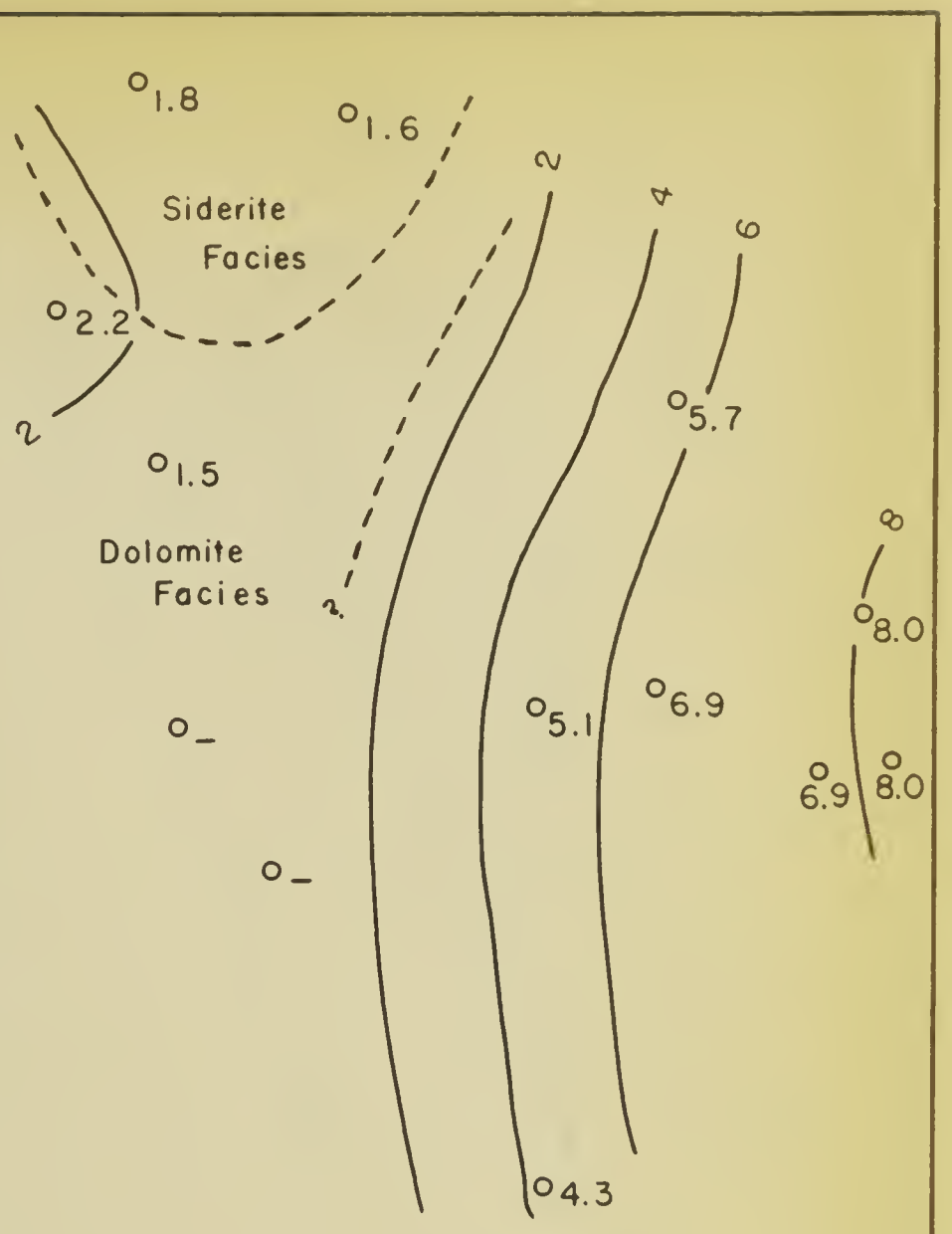
C. Mineral and Chemical Facies

An examination of the areal distribution of some of the minerals, oxides and elements within correlative units was undertaken, both as a check on the consistency of the interpretation and as an indication of the influence of bottom topography on distribution patterns. Two units were chosen for comparative purposes, the Lower Mississippian, in which the unda-facies is predominantly shale and shaly limestone, and the Upper Mississippian in which the unda-facies is predominantly crinoidal limestone.

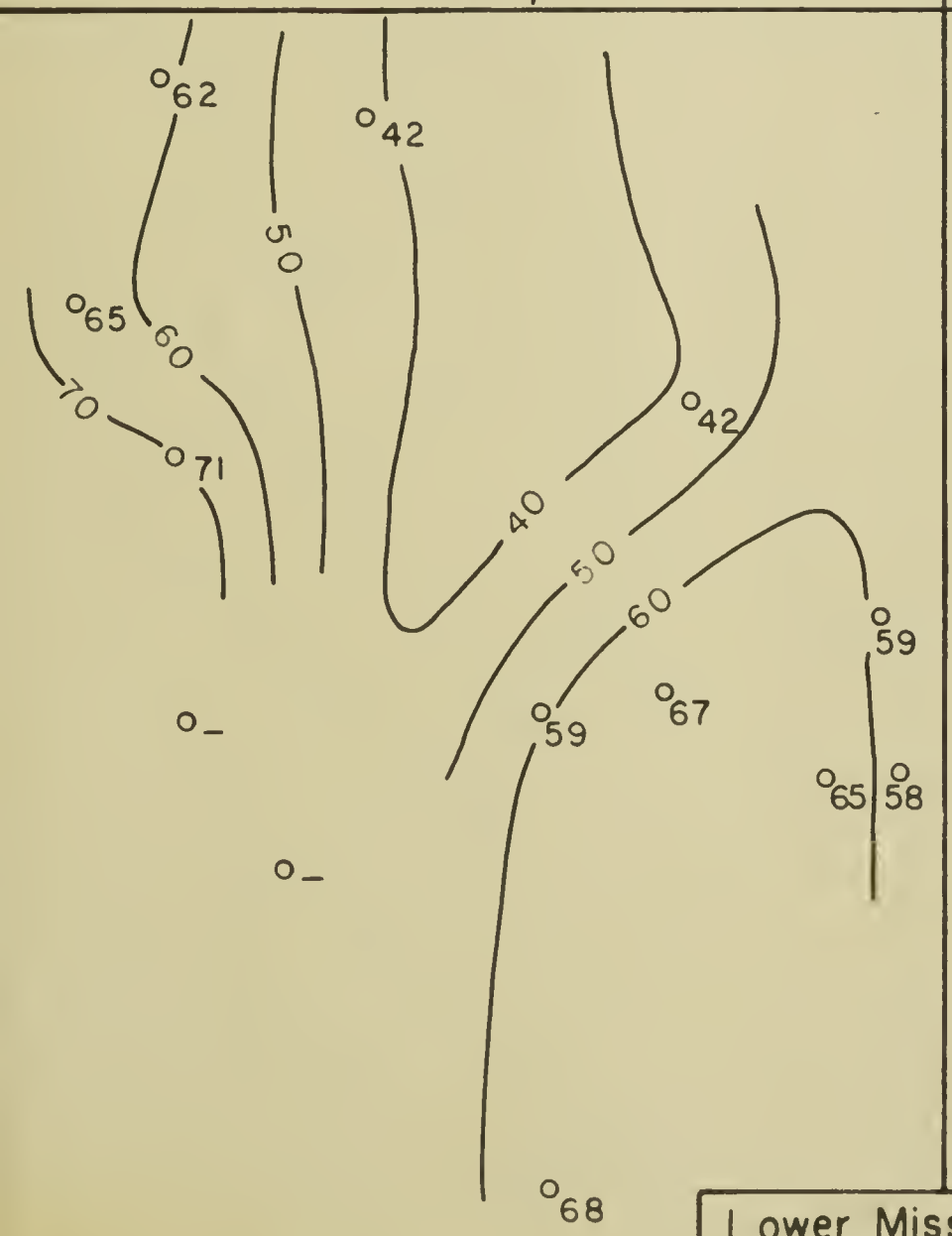
Figure 52 illustrates the areal distribution within the Lower Mississippian shales of quartz, carbonate minerals, total clay minerals and chlorite/illite ratio. The distribution of quartz appears to be markedly controlled by the position of the upper edge of the clinoform as indicated by the isopach map of Figure 50. In view of what has been said concerning the probable organic origin of the quartz, this



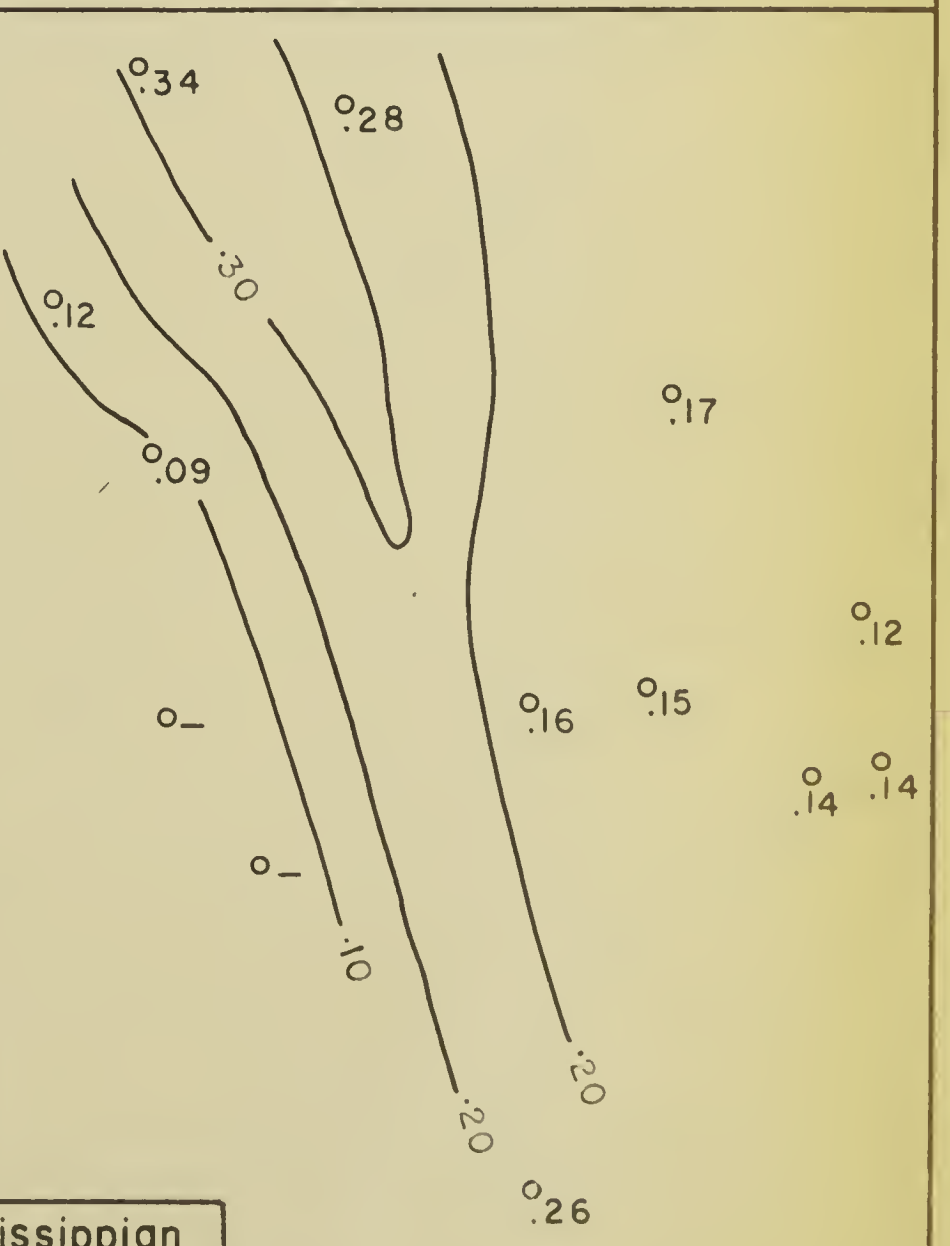
Quartz, %



Total Carbonates, %



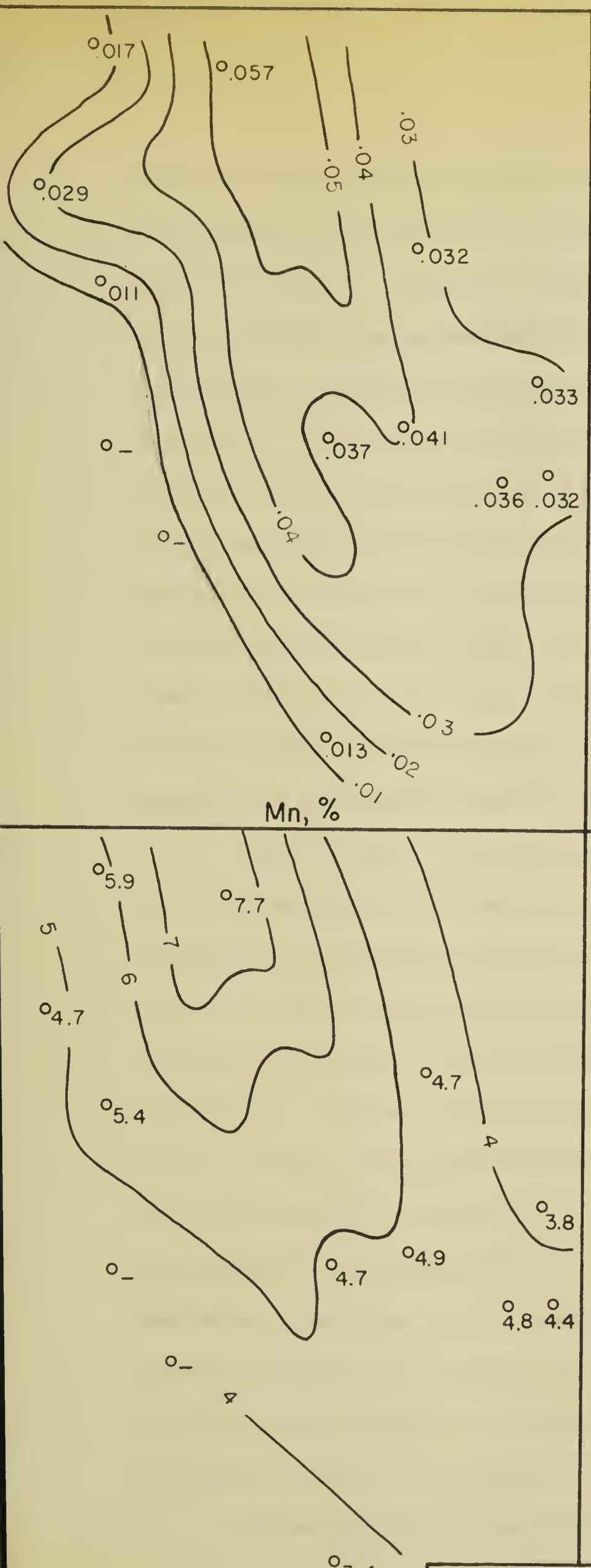
Total Clays, %

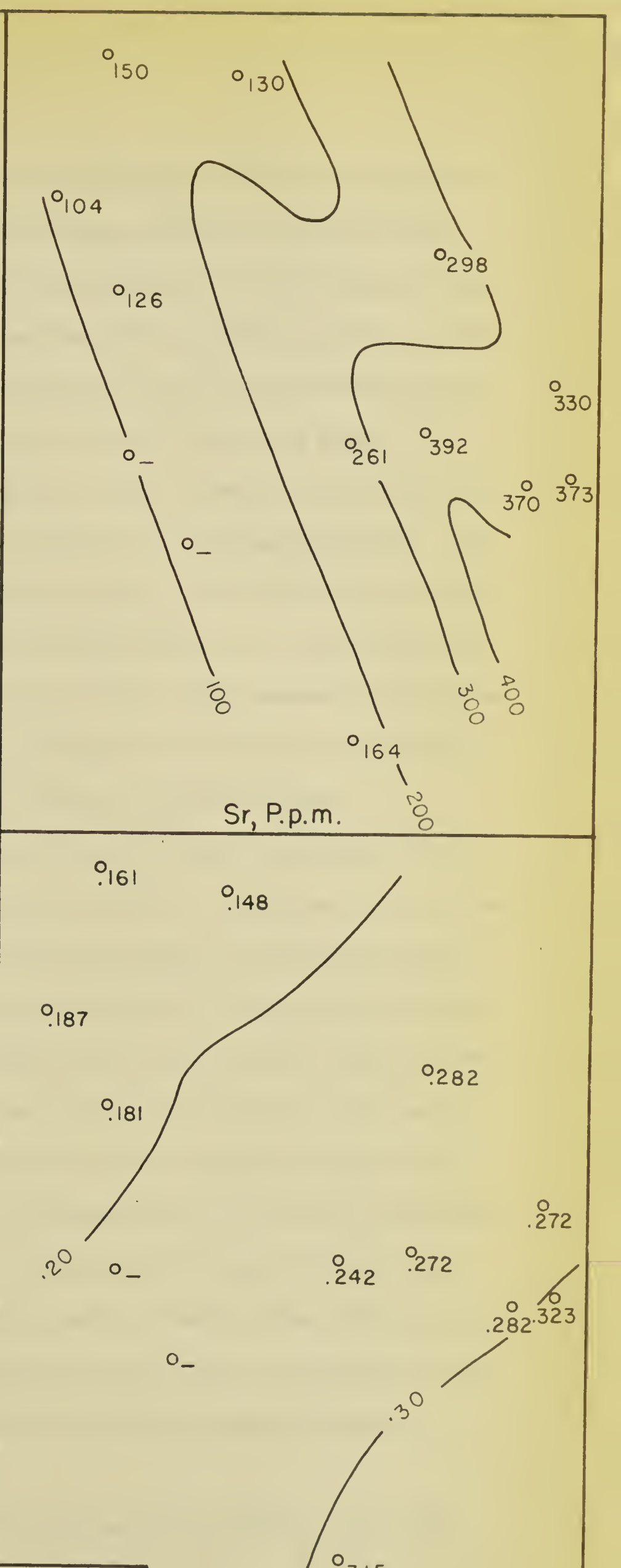


Chlorite/Illite Ratio

Lower Mississippian
Mineral Facies

FIGURE 52





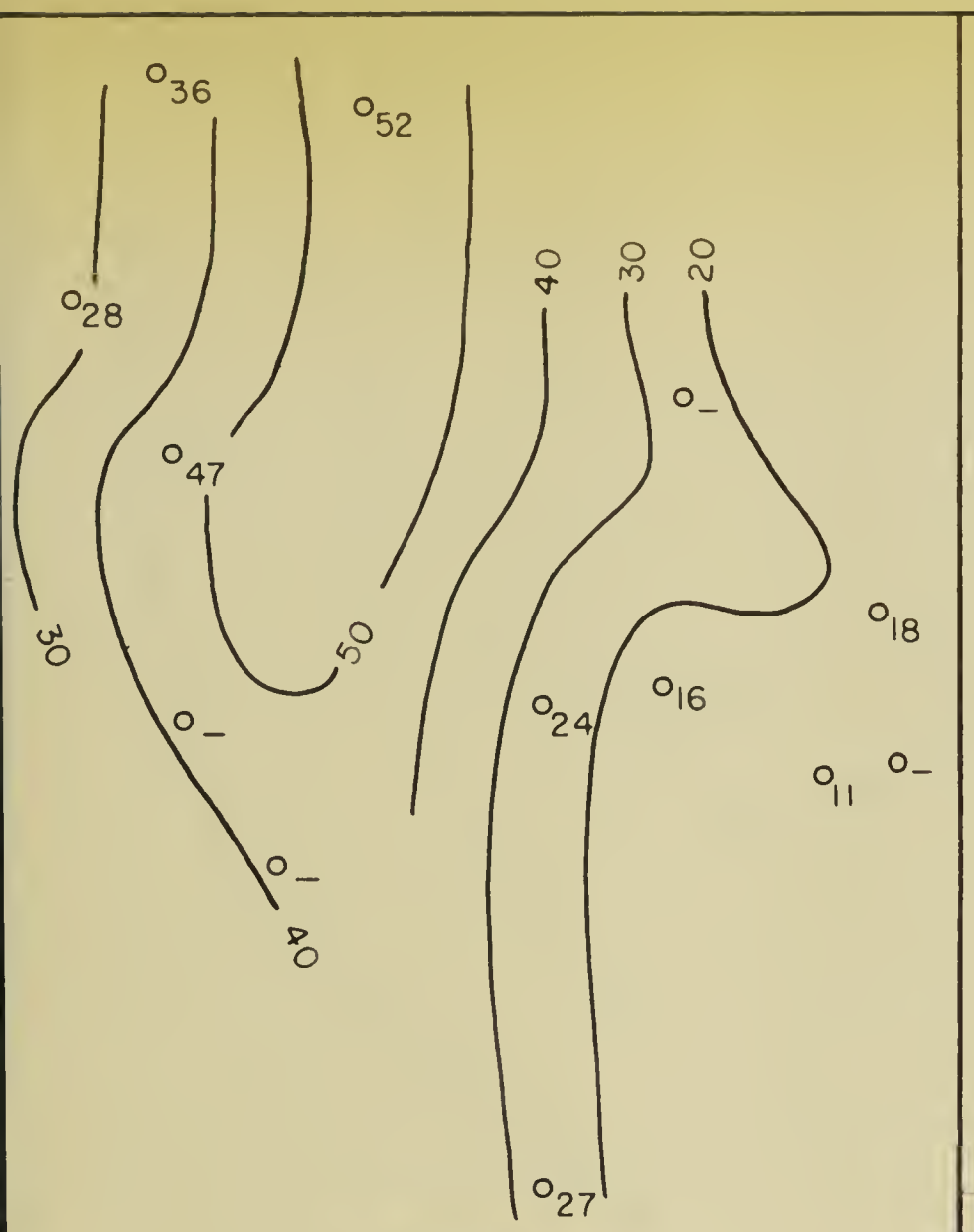
Lower Mississippian Chemical Facies

FIGURE 53

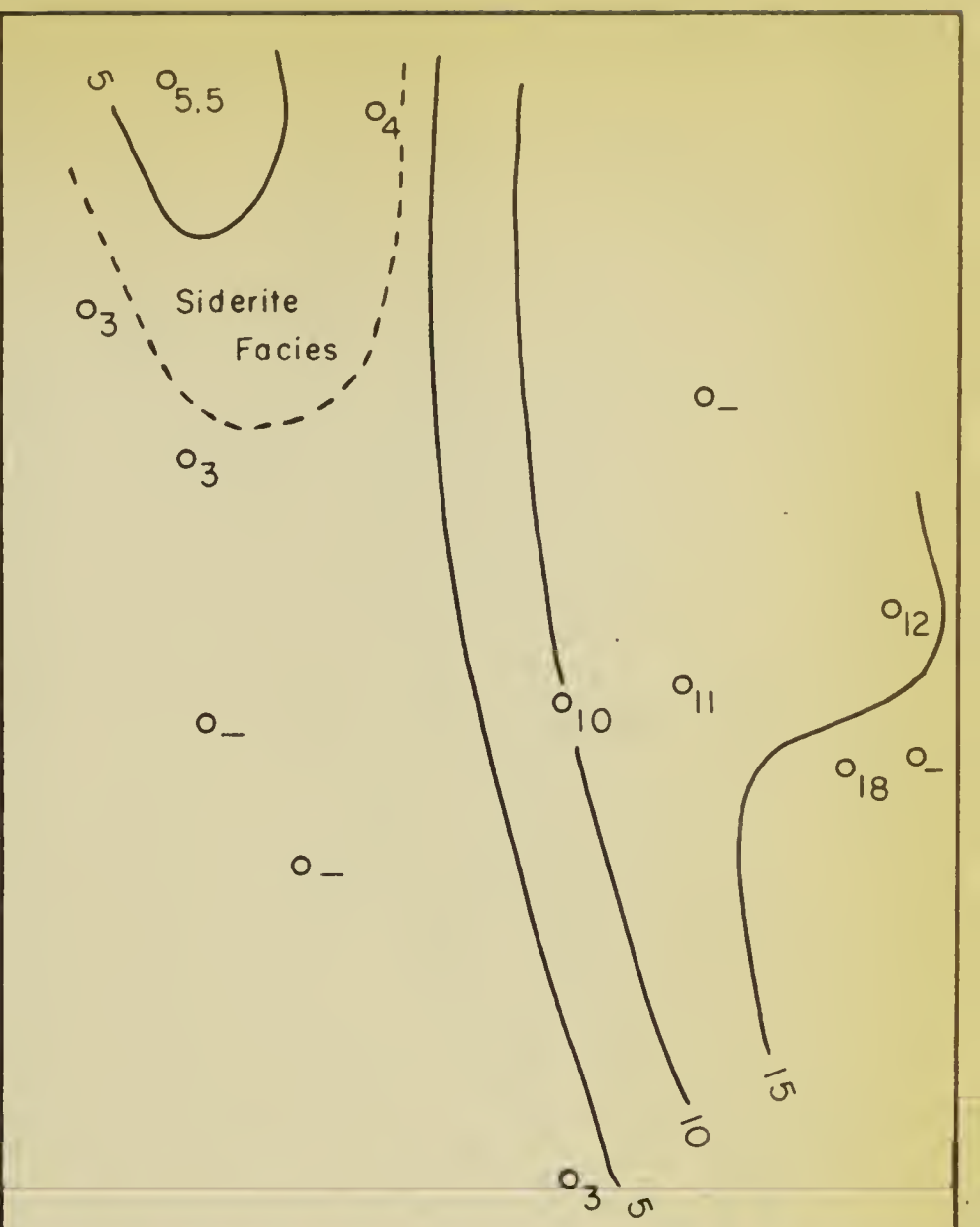
distribution pattern may be explained by upward deflection of deep currents against the clinoform, with consequent flourishing of sponge colonies and silica-secreting planktonic organisms. Winnowing of clay minerals from the clinoform edge by reflux currents of slightly concentrated waters from the shallow undaform may help to explain the high quartz content, but since the high quartz facies is also the thickest deposit in the basin, it would appear unlikely to be entirely a "lag" type of deposit. The distribution of total clay minerals is, of course, closely inverse to that of the quartz. The concentration of chlorite along the clinothem is quite unexpected however. The reason for this concentration is not clear, but certainly it is most difficult to visualize a detrital origin, as Weaver (1958) would do for most clays, for a mineral which is so closely confined to a specific depositional environment. The carbonate minerals show a decided preference for the undathem, and those present within the clinothem and fondothem are preponderantly siderite and dolomite rather than calcite.

Figure 53 shows that manganese and iron also exhibit a preference for the upper clinoform and for the clinoform-undaform boundary. Manganese shows a gradual decrease towards the shelf and a more abrupt decline down the depositional slope, in conformity with the observations of Ronov and Ermishkena (1959) regarding basinward decrease of this element. Both Mn and Fe_2O_3 also show a tendency towards a northward increase. Together with the occurrence of the Yohin Sandstone (?) in control point #5, this may well suggest the presence of a shoal or emergent element to the north of the study area as early as Lower Mississippian time. Strontium, like calcium, is preferentially concentrated within the undathem and continues to increase eastward across the undaform into presumably increasingly shallow waters. The potassium/aluminum ratio also shows a gradual shelfward increase; here, as an exception to the rule for the other facies patterns, the strike of the contours does not appear to correlate to the basin floor topography.

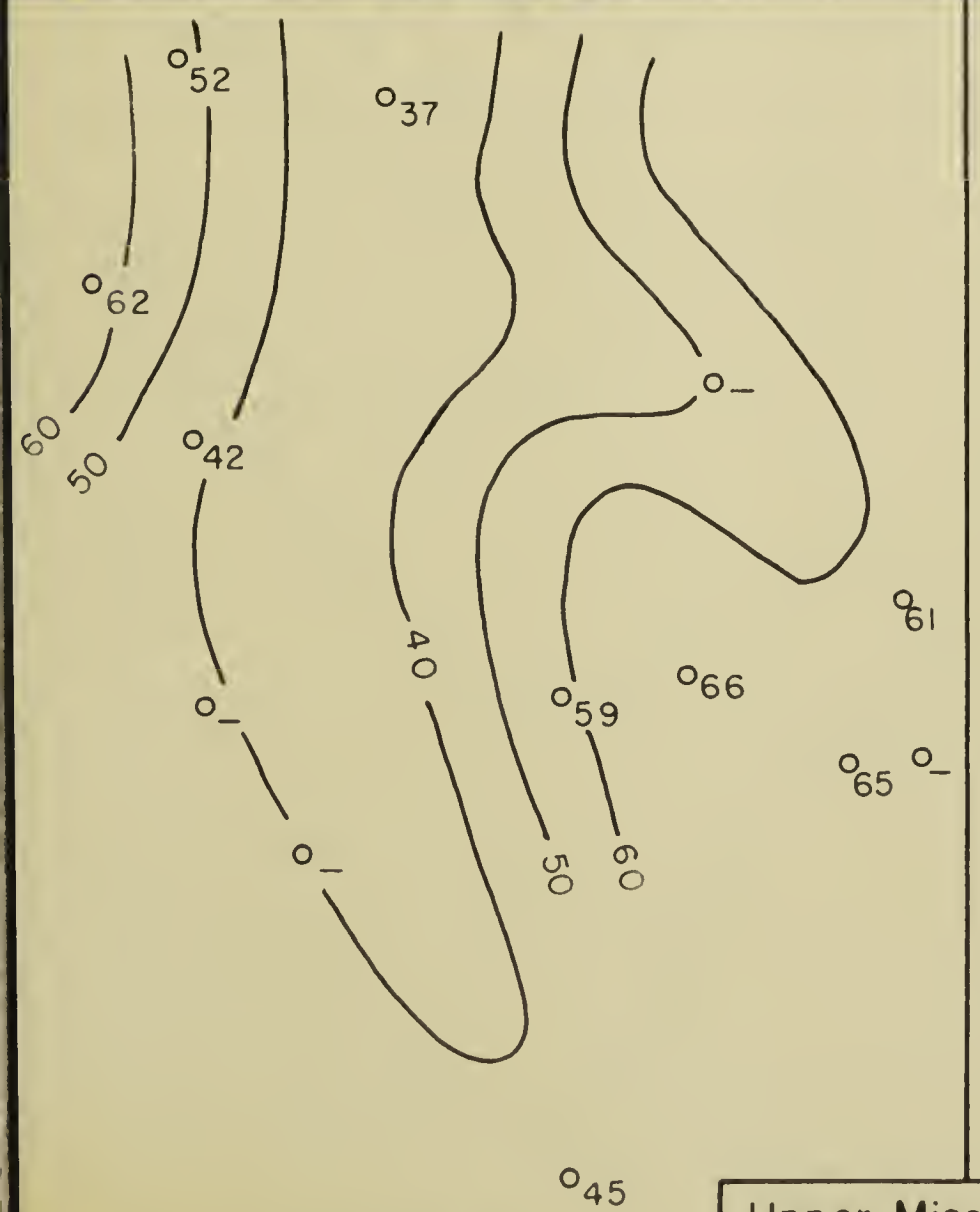
Figure 54 exhibits a close identity of mineral facies pattern of the Upper



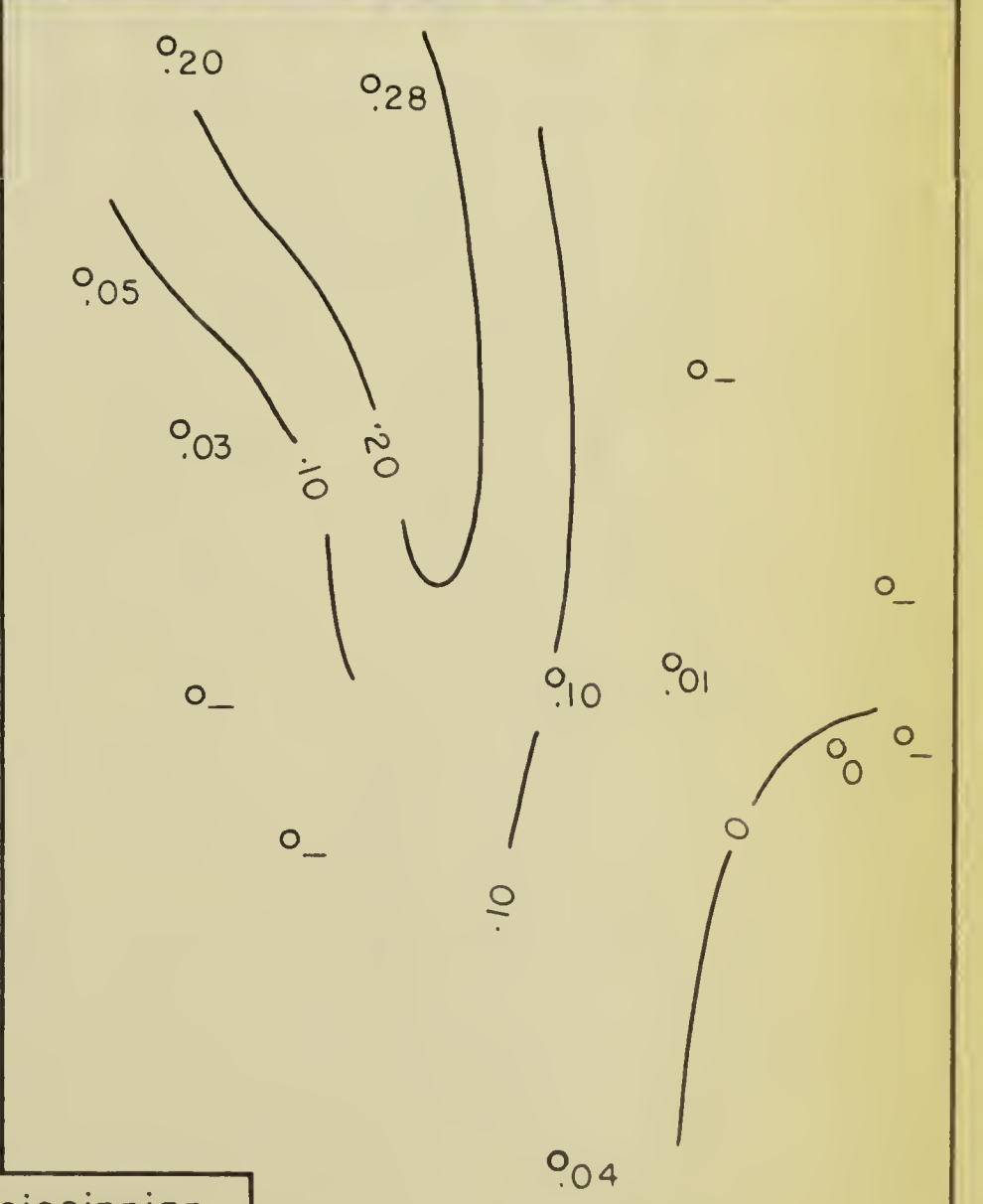
Quartz, %



Total Carbonates, %



Total Clays, %



Chlorite/Illite Ratio

Upper Mississippian
Mineral Facies

FIGURE 54

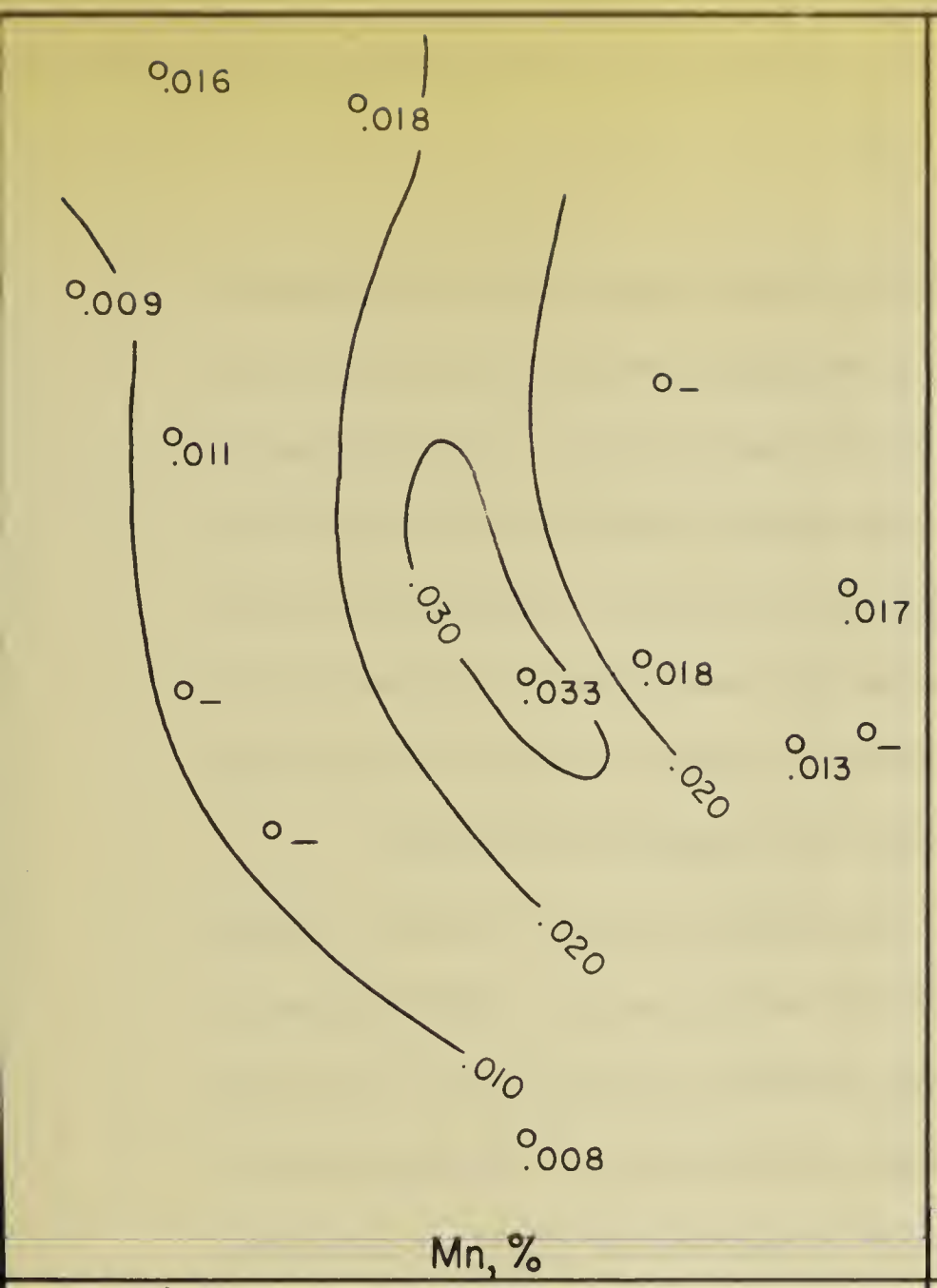

.016
.018
.009
.011
.030
.033
.018
.020
.017
.013
.020
.010
.008
Mn, %
136
246
133
131
256
362
370
100
681
113
300
400
500
600
200
Sr, P.p.m.
4.7
5.6
5
3.9
4
2.9
3
2.9
3.2
2.6
1.3
2
1.8
Fe2O3, %
.165
.154
.20
.170
.30
.40
.50
.230
.473
.282
.365
.584
.60
.359
K/Al Ratio
Upper Mississippian
Chemical Facies

FIGURE 55

Mississippian to that already observed for the Lower Mississippian. The high quartz-low clay facies has shifted to the west in conformity with the westward shift in position of the clinoform. The carbonate facies pattern is also similar to that of the Lower Mississippian shales, but the undathemic values are higher as a result of a predominantly limestone unda facies. Position of the high chlorite zone is much the same as before, but the undathem is much lower in chlorite than is that of the Lower Mississippian, reflecting the tendency towards preponderant illite formation in carbonate rocks.

The Upper Mississippian chemical facies of Figure 55 are also similar in pattern to those of the Lower Mississippian. Both the K/Al ratio and Sr are much higher in the undathemic carbonate facies than they were in the Lower Mississippian undathemic shale facies. The very high strontium concentration of 681 p.p.m. in the Debolt shales of control point #6 is of potential economic interest in view of the fact that the Debolt carbonates are highly dolomitized in this well. One could speculate that since strontium does not fit readily into the dolomite lattice it has moved into the shales during the dolomitization process. In contrast to strontium, the Fe_2O_3 and Mn values are lower than those observed in the preceding unit, and show reduced control by basin topography. This is in part due, of course, to the limited amount of shale within the undathem.

CHAPTER FIVE

RELATED PROBLEMS

A. Relationships to other Areas

The conclusion has been reached in the preceding chapter that the thin Besa River Shale of the Northern Rockies represents deep water conditions which persisted throughout upper Paleozoic time. The type section of the formation at the southern margin of the area plus the overlying Prophet cherty limestone show a considerably greater thickness of section which may be assigned to the clinothem. This indicates a depositional trend which is oblique to the trend of the Rockies, cutting across them at a very shallow angle. In support of this, Kidd (1962) and Gallant (1962) indicate that immediately north of the Peace River the undathemic barrier carbonates of the Slave Point-Presqu'ile complex are present in the mountain sections, and to the south of the Pine River the Palliser and Rundle carbonates representing shelf facies of Upper Devonian and Mississippian age make their appearance. Thus the south to north changes in Upper Paleozoic stratigraphy of the Northern Rockies repeat those observed in the east-west stratigraphic cross section of this report, but the changes take place over a much greater distance because of the small angle between the depositional strike and the strike of the mountain front.

Relationships to the north of the study area are obscured by extensive pre-Cretaceous as well as post-Laramide erosion of the Upper Paleozoic succession, suggesting persistence of positive tendencies inherited from the late Paleozoic uplift which gave rise to the Mattson clastic wedge. Givetian and Frasnian Stages of the Devonian are widely represented by the Horn River and Fort Simpson Shales, which appear indicative of relatively deep water. The Famennian however, begins to develop sand and limestone phases a short distance north of the 61st. parallel (see Douglas and Norris, 1960) heralding a shoaling tendency which becomes more

apparent in the development of the Imperial Formation farther north. Mississippian rocks extend only to about 61° 45', at which point the lower beds are represented by Yohin Sandstone and the underlying black shales.

To the east, upper Paleozoic rocks are represented by shelf facies which are successively truncated eastward by pre-Cretaceous erosion and finally terminate at their present day erosional limit against the Precambrian shield. This present day limit indicates a substantial but indeterminate amount of erosional retreat, since none of the upper Paleozoic units presently exposed there show much suggestion of near-shore facies.

Relationships to the west are more enigmatic. In the eastern part of McDame map area, some 100 miles west of control point #12, Gabrielse (1963) has mapped middle Mississippian limestones resting unconformably on Ordovician. That this is truly a positive element relative to the present study area is confirmed by the occurrence of Givetian and early Upper Devonian carbonates,similar to those of the Slave Point-Presqu'ile complex,elsewhere in the McDame area. These relationships do not, however, appear to mark a western shore line to the basin, for in the western part of the McDame area more than 15,000 ft. of eugeosynclinal chert, greenstone and argillite are present between dated Middle Devonian and mid-Mississippian carbonates. Similar eugeosynclinal Devonian successions are known in the Alaska panhandle and nearby islands (cf. Miller et al. 1959, Condon, 1961) and in the San Juan islands and Cascade Mountains of Washington (Danner, 1964). Thus the meagre data tend to support the views of Warren and Stelck (1958) regarding extensive flooding of the Western Cordilleran during upper Paleozoic time. The extremely thin and non-fossiliferous nature of the Besa River section of the Northern Rockies may be characteristic of deposition in the Cordilleran area except near areas of volcanic activity, and this may explain the lack of evidence for Middle and Upper Devonian deposition over much of this area. If so, the key to the problem may lie in the basal few hundred feet

of the exceptionally thick Slide Mountain and Cache Creek rocks, which are poorly dated and rest unconformably on the lower Paleozoic rocks as does the Middle Devonian of the interior plains.

Gabrielse and Wheeler (1961) have noted that:

"The eastern margin of the eugeosyncline is known only within the limits of a broad zone, and its location during Devono-Mississippian time is further complicated by the possibility of significant movements along faults in the Rocky Mountain and Tintina Trenches"

To speculate further on this theme, it has been noted that the Slave Point-Presqu'ile carbonate front trends southwesterly from the study area, enters the Rocky Mountains north of the Peace River and would be expected to intersect the Rocky Mountain Trench at or just south of the Peace. Is it possible that the Slave Point-Presqu'ile age carbonates of the McDame area, west of the Trench, are part of this same trend? If they are, then a left lateral strike-slip displacement in excess of 250 miles along the Trench is indicated. Certainly this suggestion is rank speculation, but if it is deserving of consideration at all then perhaps the Mississippian/Ordovician unconformity in the eastern part of McDame map area could be similarly associated with displacement of the southwesterly trending Peace River arch which would extrapolate into the Trench somewhere to the south of the Peace River.

B. Provenance of the Clay Minerals

It has already been stated or inferred that a substantial fraction of the shales including much of the quartz and all of the carbonates, pyrite and organic matter are indigenous to the basin in which the shales were deposited. Biogenic activity, direct chemical precipitation and authigenic reactions within the bottom muds were thus responsible for up to 50 percent and, in the case of the siliceous and bituminous members, more nearly 80 percent of the total mineralogical make-up of the Besa River shales. What then, is the origin and direction of provenance of the balance, which consists almost entirely of clay minerals?

Among clay mineralogists, opinion on the origin of clay minerals is divided. Those who support Weaver (1958), and the number appears to be shrinking to a minority, would assert that clay minerals are detrital in origin and not subject to any appreciable degree of alteration regardless of post-depositional environment. The exponents of Grim (1958) would largely accept the detrital origin although reserving the possibility of formation of montmorillonoids from volcanic ash, but would argue strongly for a considerable degree of diagenetic alteration in response to the depositional environment.

A detrital origin for the clay minerals poses considerable difficulty relative to the Besa River shales in terms of provenance. We have seen that the depositional topography indicates deep water to the west and therefore prohibits derivation from that direction. A source to the north is possible, with movement of the clays laterally along the depositional strike by longitudinal currents. Some of the shelf shale equivalents however, such as the Ireton Formation, extend southeasterly onto the shelf for over 500 miles from the study area, and transport of clays for this distance seems improbable. Moreover, the Ireton shales of Central Alberta display depositional slopes, as Oliver and Cowper (1963) have shown, which face west just as do those of the Besa River.

It would appear then that both the depositional slopes and the lack of any other logical provenance area suggest that the clay minerals moved into the Besa River basin from the shelf lying to the east and southeast. If it is difficult to visualize the clay minerals moving through the depositional environment of the Wabamun limestone of Northern Alberta to reach the shale basin, it becomes almost impossible to visualize them being transported through the Potlatch anhydrite of Southern Alberta, Saskatchewan and Montana. Similarly the Prairie salt and Elk Point evaporites of Middle Devonian age and the Souris River and Duperow evaporitic beds of Saskatchewan seem to provide a prohibitive low energy barrier relative to transport of detrital debris however fine.

In the face of this dilemna only two working hypotheses can be visualized.

Perhaps the clay minerals did indeed originate as volcanic ash derived from volcanic islands to the west, undergoing alteration to montmorillonitic clays and subsequently to mixed layer illite-montmorillonite and chlorite. In the high energy environment of the undaform these very fine grained alteration products would be constantly moved seaward, and the thick deposits immediately in front of unda units such as the Debolt would represent "sweepings" from the shelf.

The second working hypothesis would involve formation of the clay mineral very close to the locale where they are now found. The experiments of Hénin (1955) on synthesis of montmorillonitic and illitic clays from dilute solutions at low temperature and pressure appear to have been largely ignored. If we visualize reflux currents of slightly concentrated sea water returning from the undaform to mingle with an environment rich in opaline silica at the clinoform edge, then we have conditions which come close to duplicating the laboratory experiments of Hénin. It is not considered improbable that the clay mineral may have been formed in situ under these conditions.

The author does not care to indicate a preference for one or the other of the above working hypotheses in the absence of factual evidence bearing on differentiation of the two. Nor would it be appropriate to leave the impression that either or both mechanisms are responsible for all clay minerals. The clays are acknowledged weathering products of most rock types, and it is entirely reasonable to assume that many or even most shales are of detrital origin. The difficulty in this particular instance lies in applying such an origin to the Besa River shales, and these, it is suggested, may have an origin other than detrital.

C. Radioactive Black Shales

The mode of origin of black shales in general, and in particular of the bituminous black shales which exhibit high gamma ray activity because of their high uranium content, is highly controversial. A review of the subject is beyond the scope of this report, but a summary of the present state of uncertainty on the subject is

provided by Pettijohn (1957).

"That the black shales were deposited under anaerobic conditions is unquestioned. Whether, however, the basin of accumulation was shallow or deep and whether it was landlocked or freely connected with the sea or even only a stagnant area in the open sea has been much debated. It seems most probable that some impediment to convection currents is necessary and the best hindrance is a density stratification related to salinity differences. Such is readily obtained in a barred basin".

Two black radioactive shale units, the Exshaw Formation and the Muskwa Member of the Horn River Formation constitute, by reason of their mineralogical and geochemical distinctiveness, two of the primary correlation markers of this study. Both exhibit the same characteristics:

(a) High quartz content and low clay mineral content, with a decided preponderance of illite over chlorite.

(b) Generally low carbonate content.

(c) Low iron content but high sulphur content, i.e. most of the iron is present as pyrite.

(d) Low content of the three trace elements Mn, Rb and Sr.

(e) Black color and high uranium content as indicated by gamma ray activity.

The latter characteristics in themselves serve to identify the units over very wide areas, but as the radioactivity decreases westward and the color of the surrounding shales becomes black, we are forced to rely entirely on the mineralogical and geochemical criteria for identification. These criteria also became blurred and poorly defined in the depths of the fondoform, but they do persist far enough to enable us to assert that neither depth of water nor barring of the basin is an environmental factor controlling the deposition of these shales.

In a study of the radioactive Khadum Shale of the Caucasus, Serikov (1963) concluded that concentration of uranium occurred by the reduction of sexivalent uranium to the insoluble quadrivalent form. Because many pyritic black shales do not display anomalous radioactivity, he was forced to assume that some factor in addition to reducing bottom conditions was required. He concluded that this additional factor

was high salinity, resulting in an initially enhanced concentration of uranyl ion. Thus he states that the Khadum Shale was deposited in relatively shallow, highly saline lagoons isolated from open marine basins.

Serikov's geochemical reasoning seems sound. His description of the Khadum Shale shows however that it has a wide areal extent and is the basal phase of a shale transgression over an underlying shelf limestone. This seems inconsistent with his proposed lagoonal origin, but a stratigraphic analogy is observed to the Exshaw Shale, which is the basal phase of the Banff Shale transgression over the Wabamun Limestone of the shelf, and to the Muskwa Member of the Horn River Shale which is the basal phase of the post-Slave Point shale transgression.

It has already been indicated that the Wabamun Limestone of the shelf grades southeastward into the Potlatch Anhydrite of southern Alberta, Montana and Saskatchewan. As the seas deepened at the onset of the Banffian transgression, normal marine waters would have invaded these saline evaporating pans, and in places would have advanced over a bottom of pre-deposited evaporites. Thus in the initial stages of the advance, a highly concentrated brine would have formed beneath the normal marine waters due to density stratification. This layer would move slowly seaward in response to gentle bottom gradients, eventually reaching the shale basin itself where it crossed the undaform and flowed rapidly down the clinoform. During this latter and, because of steep bottom slopes more rapid stage of the journey, high salinity concentrations would be rapidly dissipated by mixing.

Slow mixing of this highly saline bottom layer by diffusion and turbulence would of course be taking place at all times, leading to a high supply of nutrient salts within the advancing seas. Planktonic life would flourish and preservation of planktonic debris on the highly saline bottoms would be excellent, resulting in rapid accumulation of organic matter and the consequent development of a reducing and acidic environment favourable to concentration of pyrite and uranium, but not to the

preservation of calcite detritus except in areas of very high generation. The high quartz content would indicate a flourishing of radiolarians and other silica-secreting organisms in the high nutrient waters.

This hypothesis appears to explain most of the features associated with the radioactive black shales of this study:

(1) The combination of high salinity and reducing conditions which Serikov believed necessary for the concentration of uranium in black shales.

(2) The persistence of these unique conditions over a wide range of water depths.

(3) The unique mineralogical and geochemical characteristics of these shales.

(4) The gradual disappearance of these characteristics beyond the clinoform.

(5) The unique stratigraphic characteristics of wide areal extent and a position which coincides with the basal phase of an extensive shale transgression over shelf carbonates.

In connection with the latter item, it is noted that the Duvernay Shale of Central Alberta, which is also bituminous and radioactive, is the basal phase of the Ireton transgression over the Cooking Lake Limestone. It may be argued that there is no evidence for the occurrence of evaporites within the Cooking Lake, or for that matter the upper part of the Slave Point. This is true, but both carbonates show bank development at their seaward margin which would have acted as a sill relative to the shelf to the east. Thin evaporites could well have formed only to be redissolved during the ensuing shale transgression, or alternatively the brines of the silled shelf may never quite have reached sufficient concentration for evaporite deposition to have occurred.

This hypothesis then, meets Pettijohn's (ibid) requirements of a silled basin and density stratification, but permits the critical conditions to extend out of the silled basin during the ensuing shale transgression. Accumulation of radioactive black shales could, of course, take place in isolated lagoons or even in extensive

and shallow seas which were partially landlocked and therefore of above normal salinity. Such a paleogeographic interpretation could not, however, be invoked in the case of the radioactive black shales of this study.

CHAPTER SIX

SUMMARY AND CONCLUSIONS

Returning now to the stated purposes of this study as outlined in Chapter One, we may assess the degree to which they have been fulfilled.

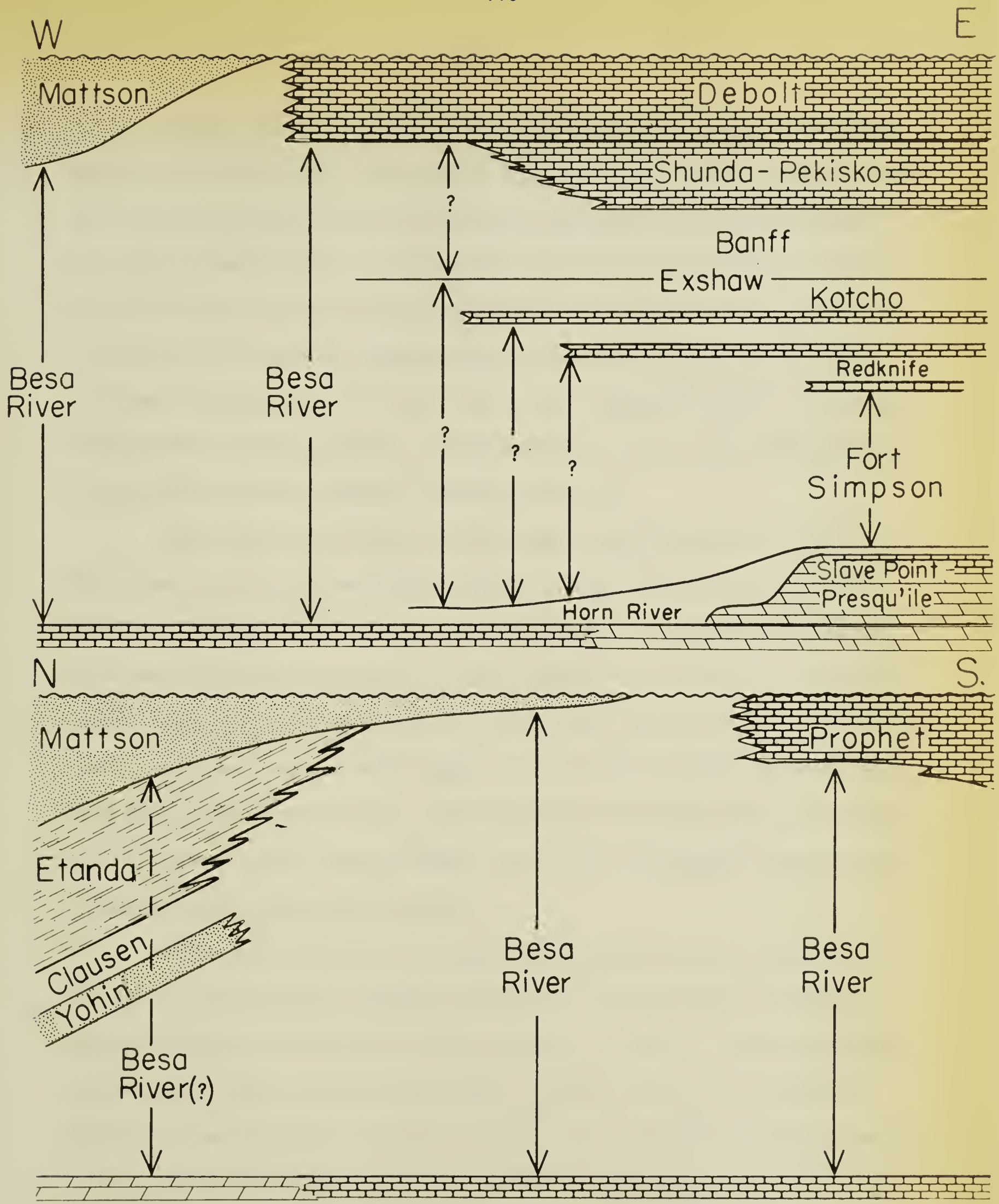
The relationship of the Besa River Shale to its lateral equivalents has been determined, with some approximation, to the Series level in eleven of the thirteen control points studied. The relationships are determinable, again with approximation, to the level of Stage in seven of the thirteen points. Considering the distances between control points and the major thickness and facies changes which are present, the results are considered to be gratifying, and favourable to the employment of mineralogical and geochemical criteria as correlation aids.

The total age range of the Besa River Formation is variable from point to point. At the positions of maximum stratigraphic development, which are those lying farthest west, the formation extends from basal Givetian to early Chesterian and thus covers a considerably wider time span than has been indicated for the type section. The base of the formation is marked over most of the study area by a carbonate unit to which no formational designation has as yet been applied, but which appears to correlate to the Chinchaga Formation and hence to the Lower Elk Point Group of Alberta. Stratigraphic buildup of carbonate above this level occurs to the east and south of the type area, and is commonly characterized by appearance of fauna of the Stringocephalus Zone. The top of the Besa River Shale is also variable in stratigraphic position, and may be taken at the base of the Prophet Limestone or, in the absence of that formation, at the base of the Mattson Formation which marks the onset of coarse clastic deposition at a level within the Chesterian Stage.

The problems of formational nomenclature are complex. It is not deemed appropriate to propose either major revisions or new terminology on the basis of a

study which is primarily mineralogical and geochemical in nature, but some comments on the problem may not be amiss. The first question which arises is whether this stratigraphic unit merits Group status. From the mineralogical and geochemical point of view Group status would certainly be appropriate. The writer believes that this may eventually prove desirable for lithological reasons as well. Thus in the Beaver River well (control point #4), the siliceous and calcareous phase below 8,500 ft. may well prove to be deserving of formational status, necessitating superior status for the Besa River. Again, in the Beavercrow well (control point #5) the Yohin (?) sandstone is overlain by black shale which is probably assignable to the Clausen Formation, and this in turn is overlain by sandy black shale which appears to represent the Etanda Formation. It would seem that the affinity of these formations to the Besa River could be best described by including them within a Besa River Group.

The question of how widely the term Besa River should be applied, particularly to the east and south of the type section, is also pertinent. The natural limit here would seem to be the limit of recognition of the Exshaw Shale as a lithologic unit. Beyond this point the Upper Devonian and Lower Mississippian Series would be no longer divisible by conventional means. Such a limit would pass immediately west of control points #3 and #8 of this study. This proposal would, however, suffer the serious disadvantage of leaving unnamed the pre-Exshaw shales to the west of the shaleout of the Jean Marie Member of the Redknife Formation, which has apparently been taken as the limit of Fort Simpson Shale by Belyea and McLaren (1962). Also left in limbo would be the combined shale equivalents of Banff, Pekisko and Shunda Formations. Perhaps, therefore, the terms Upper Besa River and Lower Besa River could be extended to cover this gap. Certainly some agreeable if arbitrary boundary between the Fort Simpson and Besa River Formations must be defined, since the introduction of a new term at each limestone shaleout level would scarcely prove workable. The nature of this problem is illustrated in the schematic east-west and north-south sections of Figure 56.



Schematic W-E and N-S Cross Sections Illustrating Nomenclature Problems

FIGURE 56

Finally, the paleogeographic and tectonic interpretations arrived at in this study are relatively simple. The very thin Besa River sections of the Northern Rockies are fondathemic deposits representing deep water conditions which persisted from Givetian to Chesterian time. Thicker shales to the east are clinothemic in nature, with the thickest section of each stratigraphic interval occurring at the top of the clino slope, and a westward progradation of younger clino units over older. The undathem is represented in the study area by reef complexes (Slave Point-Presqu'ile), blanket clastic limestones (Debolt), and by calcareous shales with interbedded limestones which indicate a reasonably shallow water origin.

The comparatively slight westward migration of the depositional profile from Givetian through Upper Mississippian time suggests a high degree of tectonic stability. Changes in depth of water in the fondoform are indicated by differences in the magnitude of depositional slope from unda-to fondo-environment, but whether these changes were due to epeirogenic or eustatic influence is not known. The Mattson clastic wedge, on the other hand, suggests a major tectonic uplift to the north of the study area in late Paleozoic time, and the presence of turbidite sands in the northern part of the area as early as about Pekisko time (Yohin (?) sandstone) suggests an even earlier activation of this positive element.

Although this study has not been directed towards economic ends, some of the results obtained do have economic implications. The most apparent of these is that the thickness of the Horn River Shale appears to be directly related to proximity to Slave Point-Presqu'ile barrier carbonates. Similarly, proximity to the Debolt shaleout can be predicted on the basis of isopach, plus mineralogical and geochemical criteria. While the economic significance of this is not evident as yet, the eventual discovery of productive units along this major facies change would not be surprising. The possible presence of undathemic equivalents of sands such as the Yohin to the north of the study area is worthy of mention, since these may not exhibit the same

high degree of silica cementation as the clinothem and fondothem equivalents. The fact that the Besa River Shale is divisible into a number of units on the basis of mineralogical and geochemical criteria may have importance relative to the solution of structural problems in drilling in the foothills belt. Finally, it would be the writer's contention that any contribution to the understanding of depositional processes will, in the long term, be of assistance to the perceptive geologist in the task of locating hydrocarbon reserves. It is not difficult to foresee a future in which something more than hand lens, hammer and binocular microscope will be regarded as tools adequate to this task.

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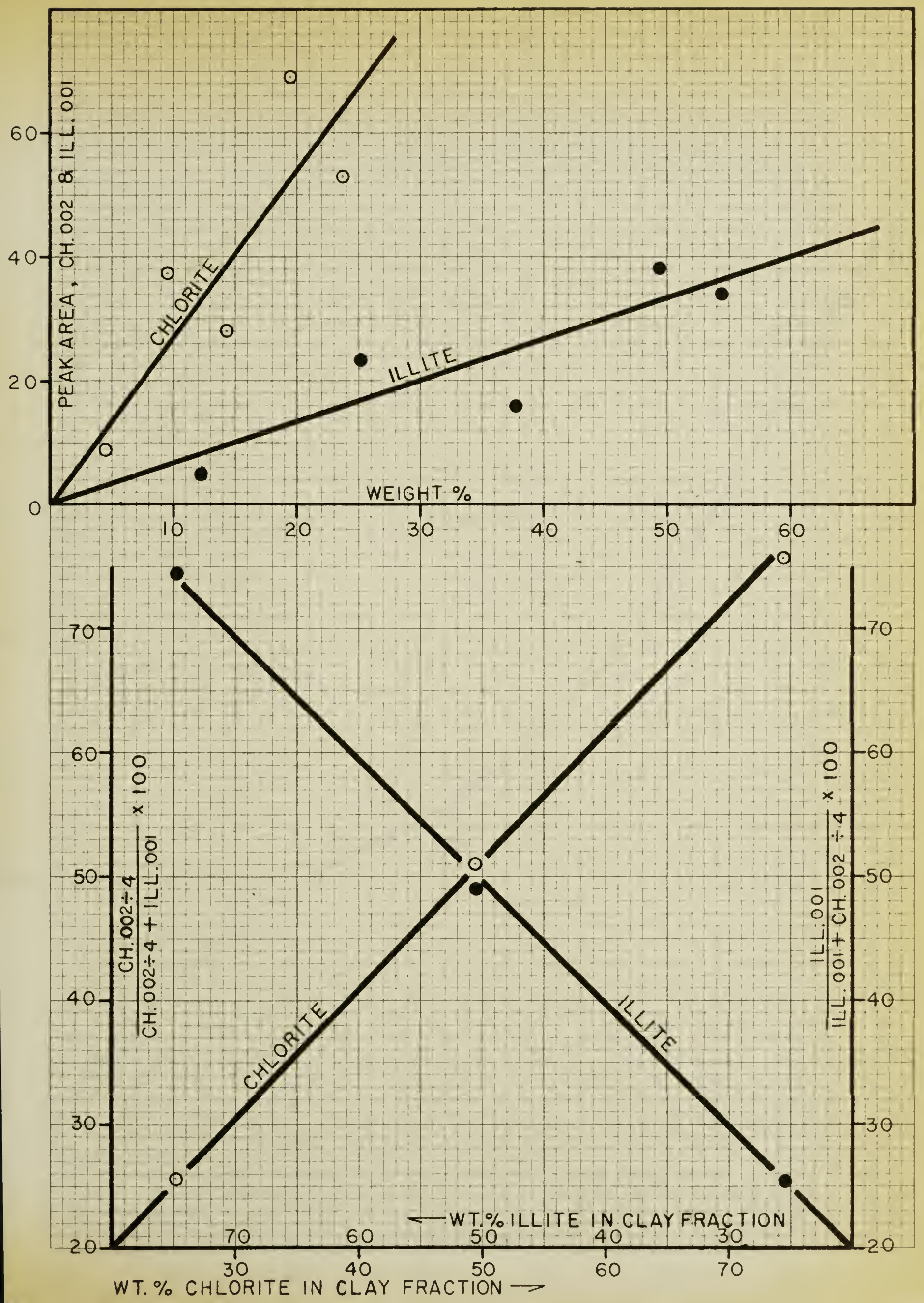
APPENDIX A

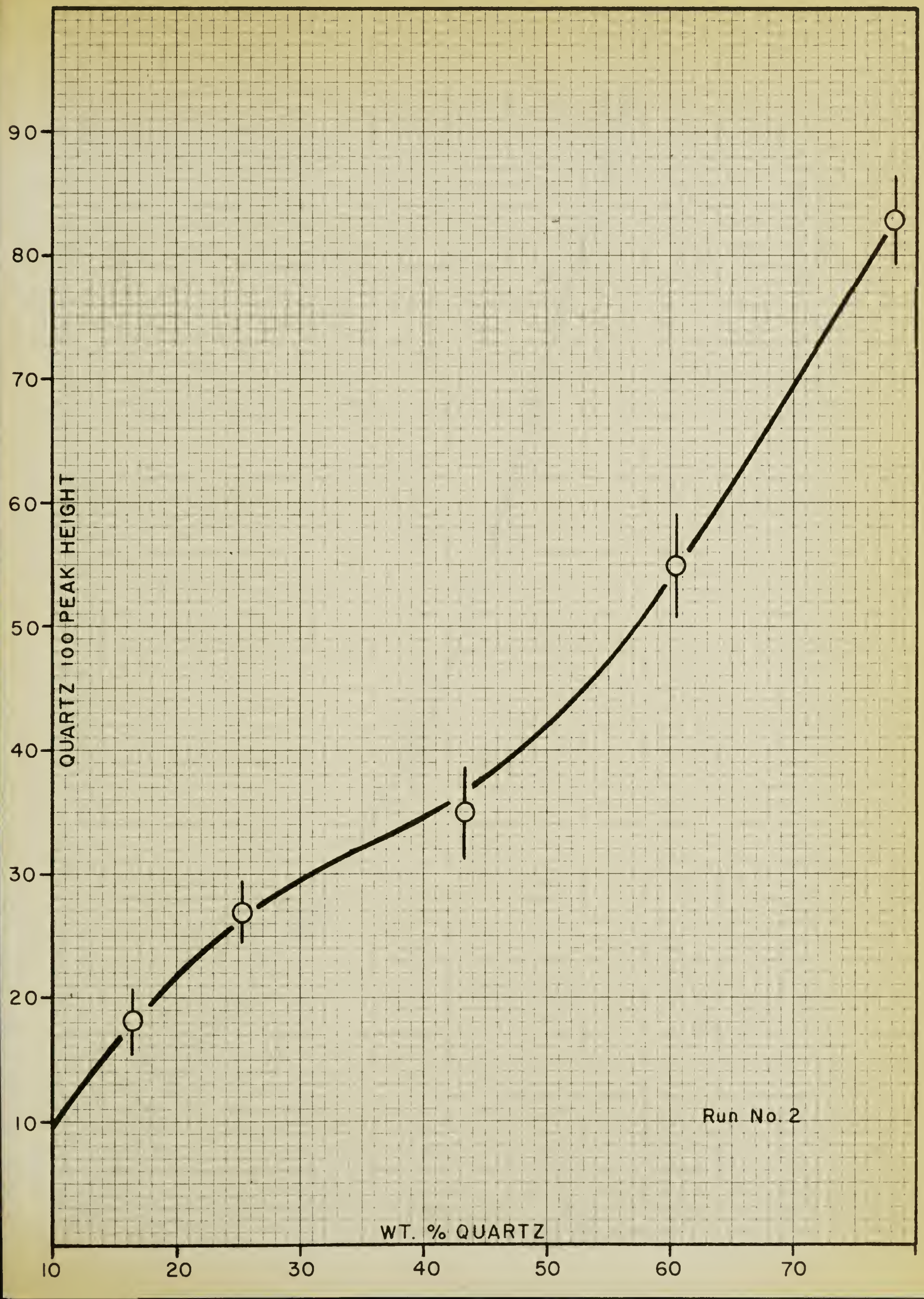
TYPICAL CALIBRATION CURVES FOR SEMI-QUANTITATIVE MINERALOGICAL DETERMINATIONS BY X-RAY DIFFRACTION

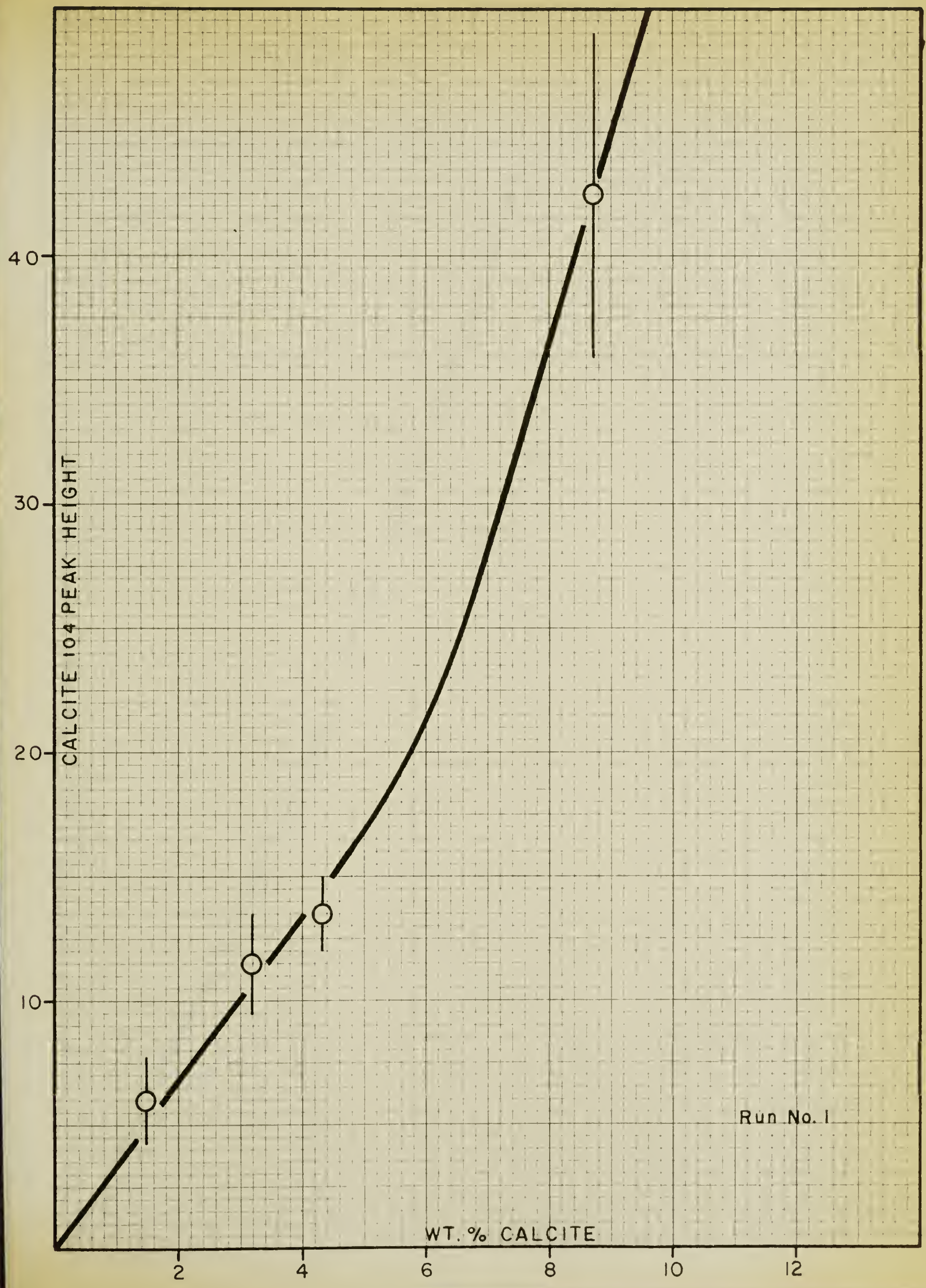
APPENDIX A

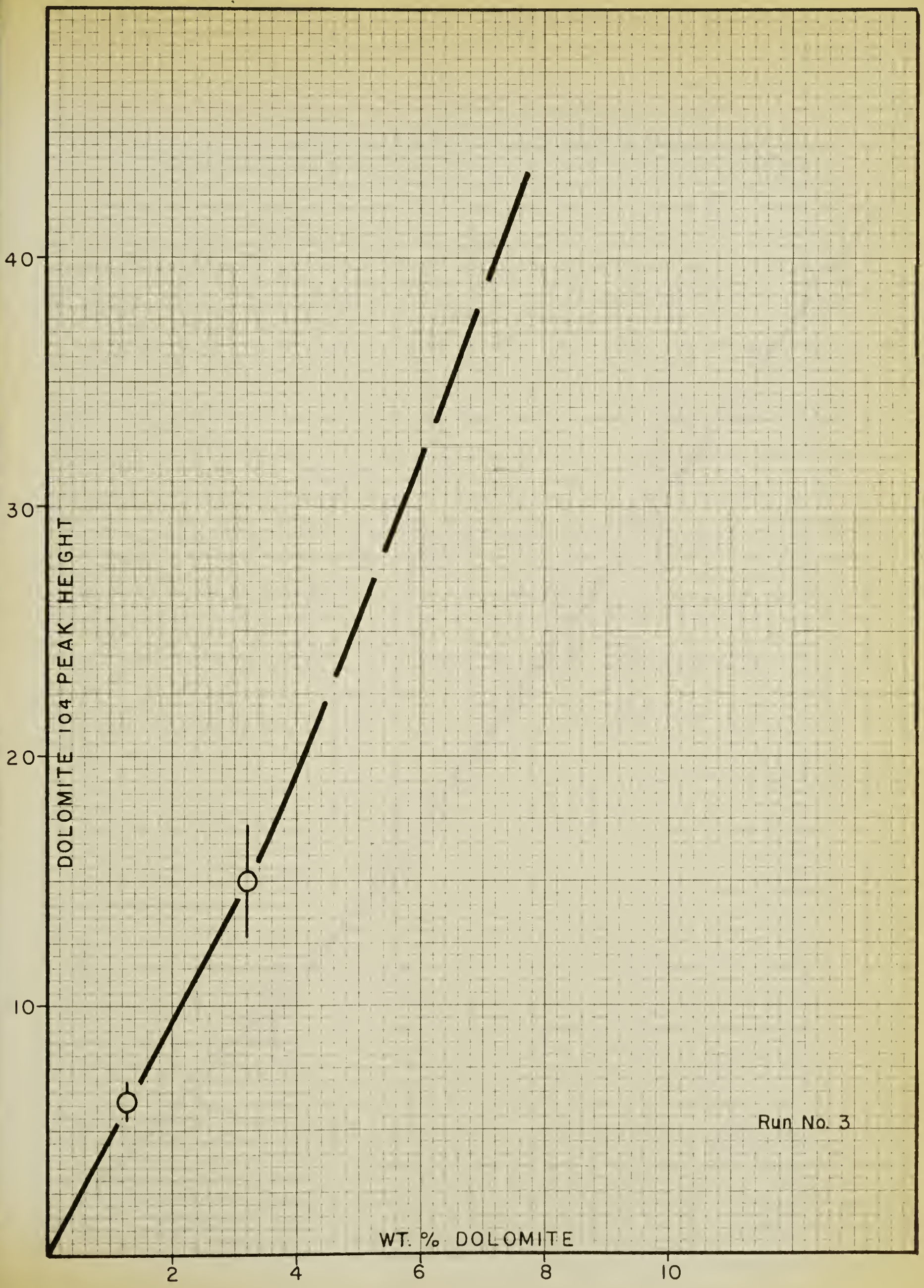
The calibration curves for chlorite and illite, shown in the upper half of page II, exhibit an unsatisfactory scatter which is attributed to differing degrees of orientation from one briquet to another. The curves are useful however, in demonstrating that the diffracting power of the chlorite 002 planes is four times greater than that of the illite 001 planes. We can use this information to determine the percentage of each mineral in the clay fraction through the use of normalized area ratios. As the curves of the lower half of page II show, we can thus achieve an accuracy of relatively high order on "artificial" shales made from known amounts of chlorite, illite and quartz. This "normalized area ratio" method was used to determine the proportions of the two minerals in each unknown sample, and the total clay fraction was determined by difference, as indicated in the text.

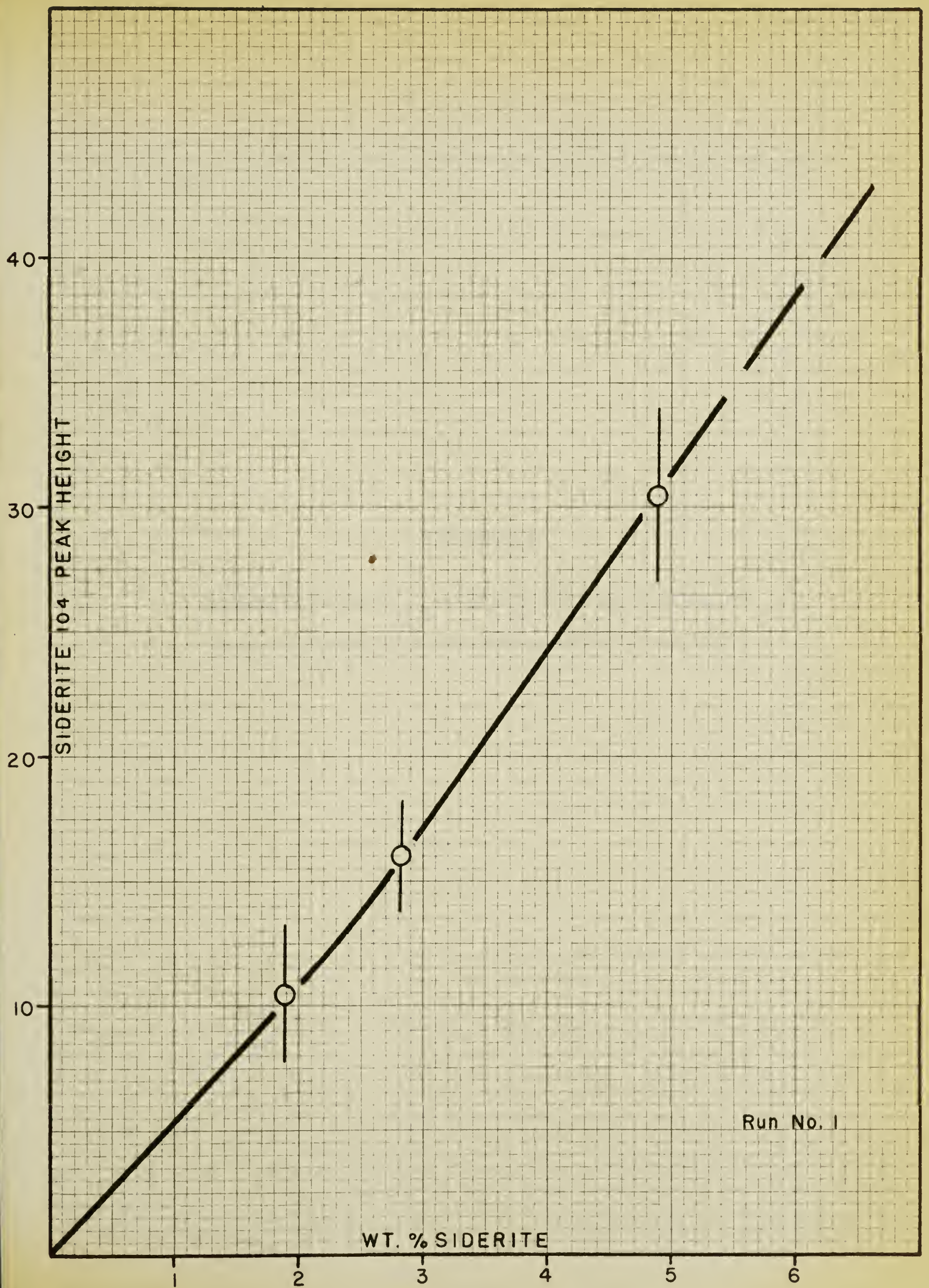
The calibration curves for quartz, calcite, dolomite and siderite are shown on pages III, IV, V and VI respectively. The peak height has been measured relative to background. Units of measurement are tenths of an inch as recorded using a multiplier setting of 4 and a scale factor of 1.


PEAK AREA, CH. 002 & ILL. 001
CHLORITE
ILLITE
WEIGHT %
0
20
40
60
10
20
30
40
50
60
70
CH. 002÷4 / CH. 002÷4 + ILL. 001 × 100
ILL. 001 / ILL. 001 + CH. 002 ÷4 × 100
CHLORITE
ILLITE
← WT. % ILLITE IN CLAY FRACTION
WT. % CHLORITE IN CLAY FRACTION →


90
80
70
60
50
40
30
20
10
QUARTZ 100 PEAK HEIGHT
10
20
30
40
50
60
70
WT. % QUARTZ
Run No. 2


40
30
20
10
CALCITE 104 PEAK HEIGHT
2
4
6
8
10
12
WT. % CALCITE
Run No. 1


40
30
20
10
DOLOMITE 104 PEAK HEIGHT
2
4
6
8
10
WT. % DOLOMITE
Run No. 3


40
30
20
10
SIDERITE 104 PEAK HEIGHT
WT. % SIDERITE
1
2
3
4
5
6
Run No. 1

APPENDIX B

CORRECTION OF Al_2O_3 AND SiO_2 DETERMINATIONS BY X-RAY FLUORESCENCE FOR MASS ABSORPTION EFFECTS

APPENDIX B

Correction of Al_2O_3 and SiO_2 Determinations by X-ray Fluorescence for Mass Absorption Effects.

In X-ray fluorescence, it is generally assumed that the amount of secondary radiation measured is directly proportional to the amount of the given element present in the sample. Thus, by comparison with a standard of known composition, one can directly determine the amount present in the unknown:

$$(1) \qquad \% Ax = \% Ast. \cdot \frac{c.p.s.\ x}{c.p.s.\ St.}$$

where % Ax = % element A in the unknown

% Ast. = % element A in the standard

c.p.s. x = counts per second for A radiation in the unknown

c.p.s. St. = counts per second for A radiation in the standard

In practise, errors are introduced by virtue of the fact that the mass absorption co-efficients (μ_x and μ_{st}) of the unknown and standard may differ, i.e. the two samples may permit differing proportions of the secondary characteristic radiation to exit from the sample. If these mass absorption co-efficients were known, then this effect could be corrected for by modifying Equation (1) to :

$$(2) \qquad \% Ax = \% Ast. : \frac{c.p.s.\ x}{c.p.s.\ St.} \cdot \frac{\mu_x}{\mu_{st.}}$$

where μ_x = Mass absorption co-efficient of the unknown for the specific wavelength under consideration.

μ_{st} = Mass absorption co-efficient of the standard for the same specific wavelength.

The mass absorption coefficients will be different for each characteristic wavelength, and will depend in each instance on the chemical composition of the sample. If the chemical composition of the sample is known, then its mass absorption co-efficient can be calculated as the sum of the products of the mass absorption co-

efficients of each oxide with the weight fraction of the oxide; for comparative purposes we can substitute weight percent for weight fraction:

(3) $\mu \times A = (\mu_{Ao} . \% A) + (\mu_{Bo} . \% B) + (\mu_{Co} . \% C)$ .....

where $\mu \times A$ = Mass absorption co-efficient of the sample for A radiation.

$\mu_{Ao}, \mu_{Bo}, \mu_{Co}$ = Mass absorption co-efficients of the oxides of A, B, C ..... for A radiation.

%A, %B, %C = Weight percent of oxides A, B, C .....

At first sight the problem appears incapable of solution since the chemical composition which controls the mass absorption co-efficient is, in the case of the unknown sample, what one is trying to determine. Let us look however (Table A) at the mass absorption co-efficients of the various oxides for the different characteristic wavelengths.

TABLE A

	Al (8.34 Å)	Si (7.12 Å)	K (3.74 Å)	Ca (3.36 Å)	Fe (1.94 Å)
μ Al_2O_3	89	228	42	32	5
μ SiO_2	102	65	42	35	6
μ K_2O	148	96	97	85	23
μ CaO	168	110	91	80	23
μ Fe_2O_3	264	179	35	28	37
μ Residue	77	48	7	5	1

The "residue" column of this table is taken as one half of the mass absorption of oxygen, assuming that water, carbon dioxide and organic compounds will account for most of the residue in shales.

From this table it is evident that whether a shale is siliceous or clayey will not affect the mass absorption relative to K, Ca or Fe, since SiO_2 and Al_2O_3 have almost

identical absorption co=efficients for these wavelengths. Similarly, calcareous shales will behave the same as highly illitic shales, since CaO and K_2O have similar absorption characteristics. It is evident then, that for most shales the estimation of K, Ca and Fe through the use of the simple relationship of equation (1) will be quite accurate, and experience shows that this is indeed the case.

In contrast to this, the absorption of Si radiation by Al_2O_3 is very high, and we can anticipate that very clayey shales would produce spuriously low estimates for the silicon content relative to siliceous shales if equation (1) were used. Similarly, variations in chemical makeup will quite obviously affect the determination of aluminum. The application of equation (1) to Al and Si does, nevertheless, give us a first approximation of these elements or their oxides which includes the error due to differences in absorption characteristics between unknown and standard. Using this first approximation plus the reasonably accurate determination of K_2O, CaO and Fe_2O_3 we can calculate the mass absorption co-efficient of the unknown to a first approximation and, since the chemical composition and therefore the mass absorption co-efficient of the standard is known, we can apply equation (2) to arrive at a new estimate of the Al_2O_3 and SiO_2 content. This procedure can be reiterated indefinitely; in practise the reiteration was continued until successive corrections fell within the predetermined standard deviation for repeat runs on the same sample.

This reiterative procedure was programmed into Fortran IV language for the I.B.M. 7040 Computer by Mr. D. Simpson of the Computer Science Faculty University of Alberta, and is on file as Program 450006.

APPENDIX C

CALIBRATION CURVES FOR X-RAY FLUORESCENCE DETERMINATIONS, CHEMICAL ANALYSES OF STANDARDS, AND TYPICAL FLUORESCENCE OPERATING CONDITIONS.

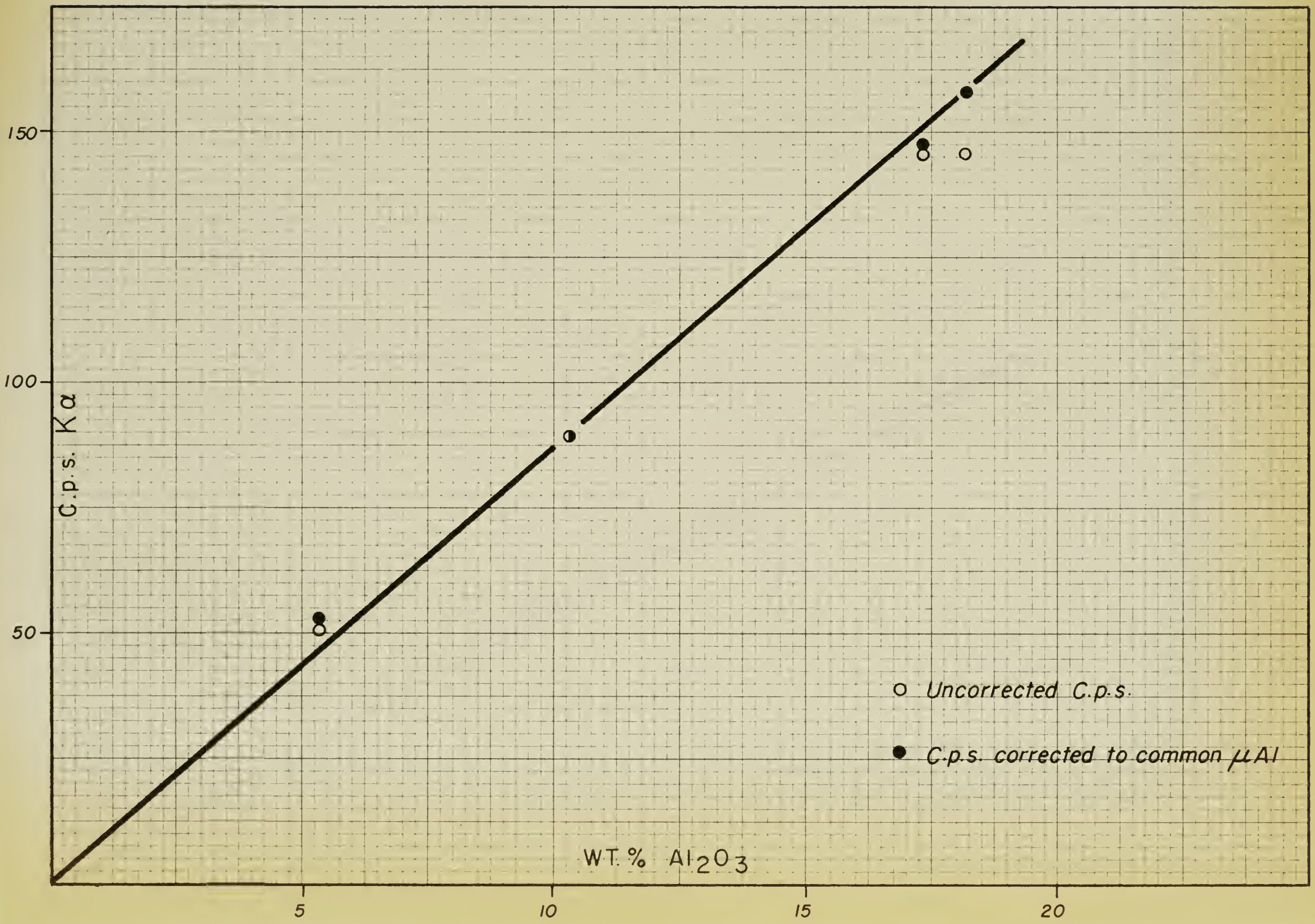
APPENDIX C

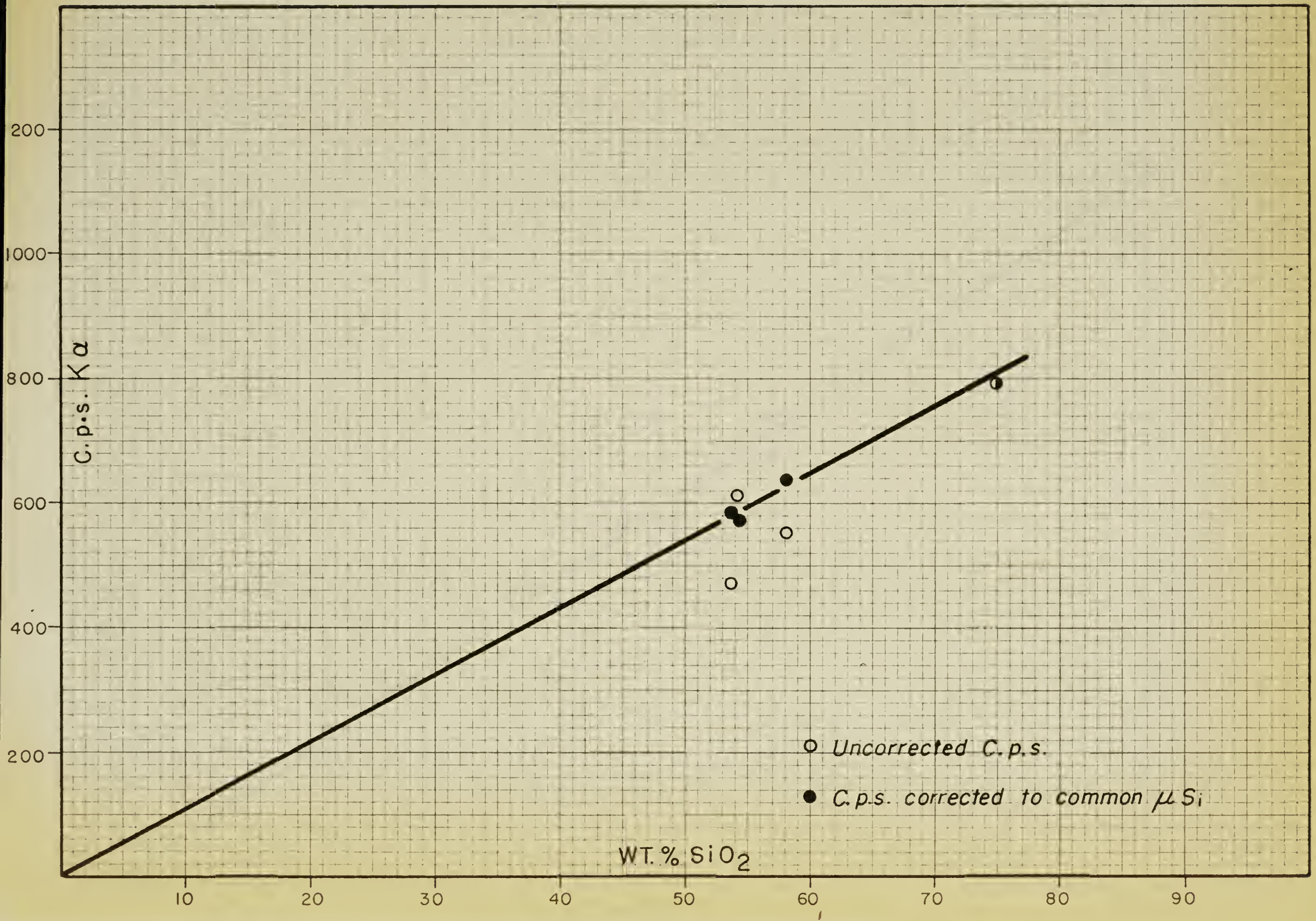
Pages XI and XII show calibration curves for Al and Si respectively, expressed in terms of the oxides of those elements. In addition to the uncorrected counting rate, the counting rate for each standard corrected to the mass absorption characteristics for one arbitrarily selected standard has been indicated. It will be seen that the uncorrected counts show a rather poor fit to a linear relationship, but that the corrected counting rates fit such a relationship quite well.

The calibration curves for K, Ca and Fe, also expressed in terms of the oxides are shown on pages XIII, XIV and XV respectively. Here the rates as corrected to a common mass absorption co-efficient have not been shown, since they are virtually coicident with the uncorrected rates, except in the case of iron which would, if corrected, show a somewhat steeper slope because of self-absorption.

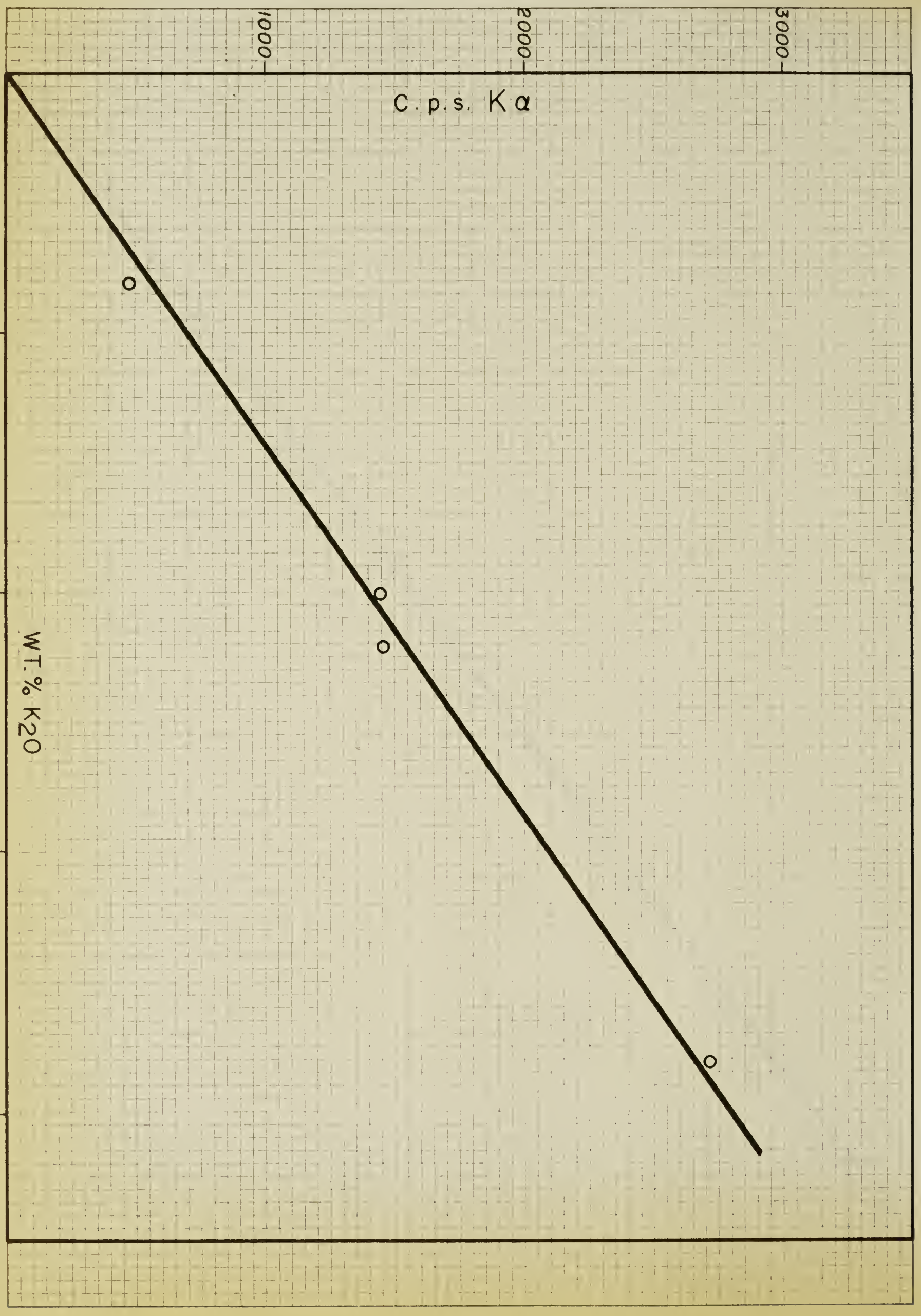
Page XVI shows chemical analyses of the four shales employed for construction of calibration curves. Standards R 56 and R 57 are Cretaceous shales from the Wapiabi Formation. Standards R 66 and R 67 are from the Besa River Formation of the study area.

Page XVIII shows typical operating conditions used in the X-ray fluorescence analyses.

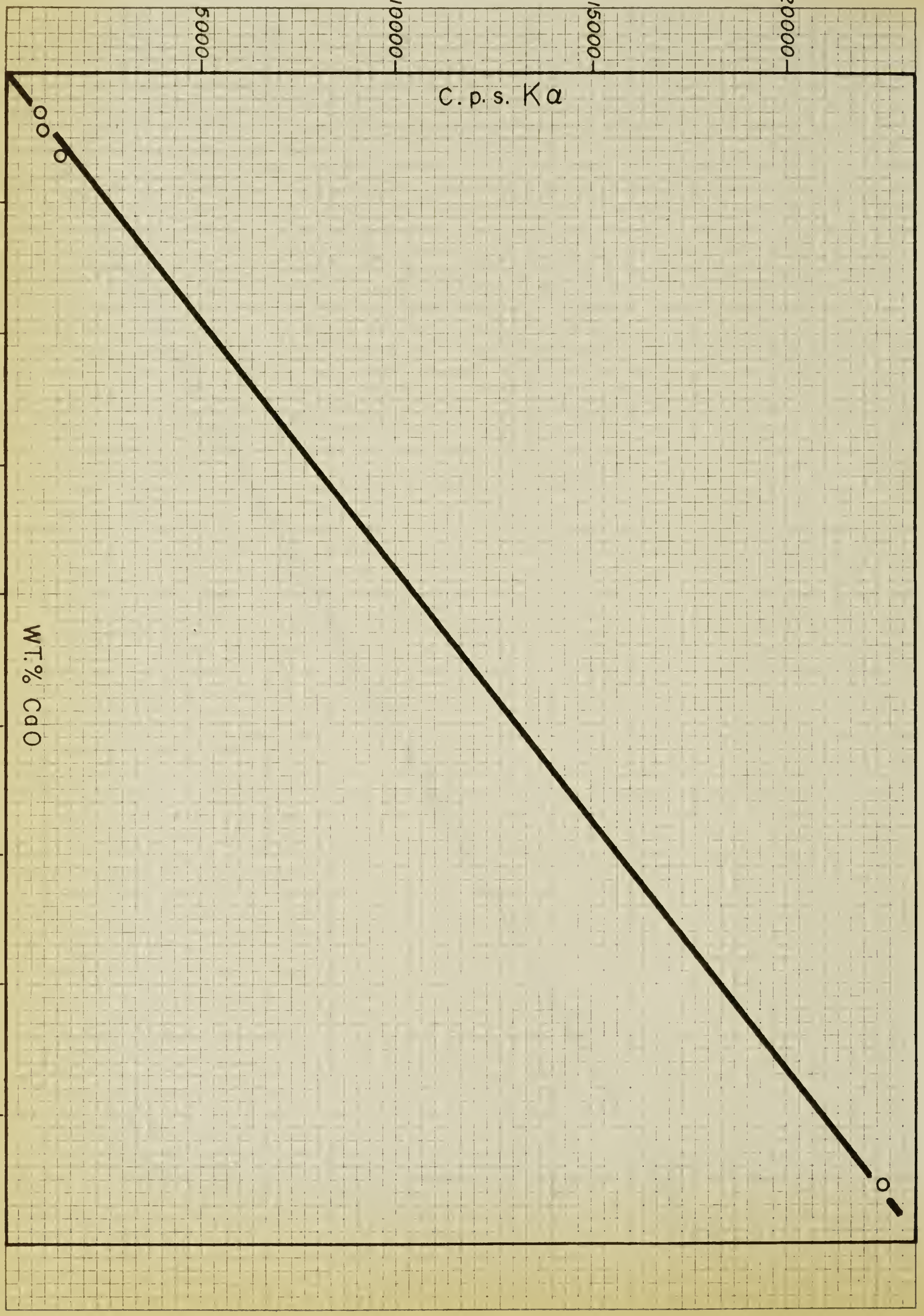

150
100
50
C.p.s. Kα
5
10
15
20
WT. % Al_2O_3
Uncorrected C.p.s.
C.p.s. corrected to common μAl

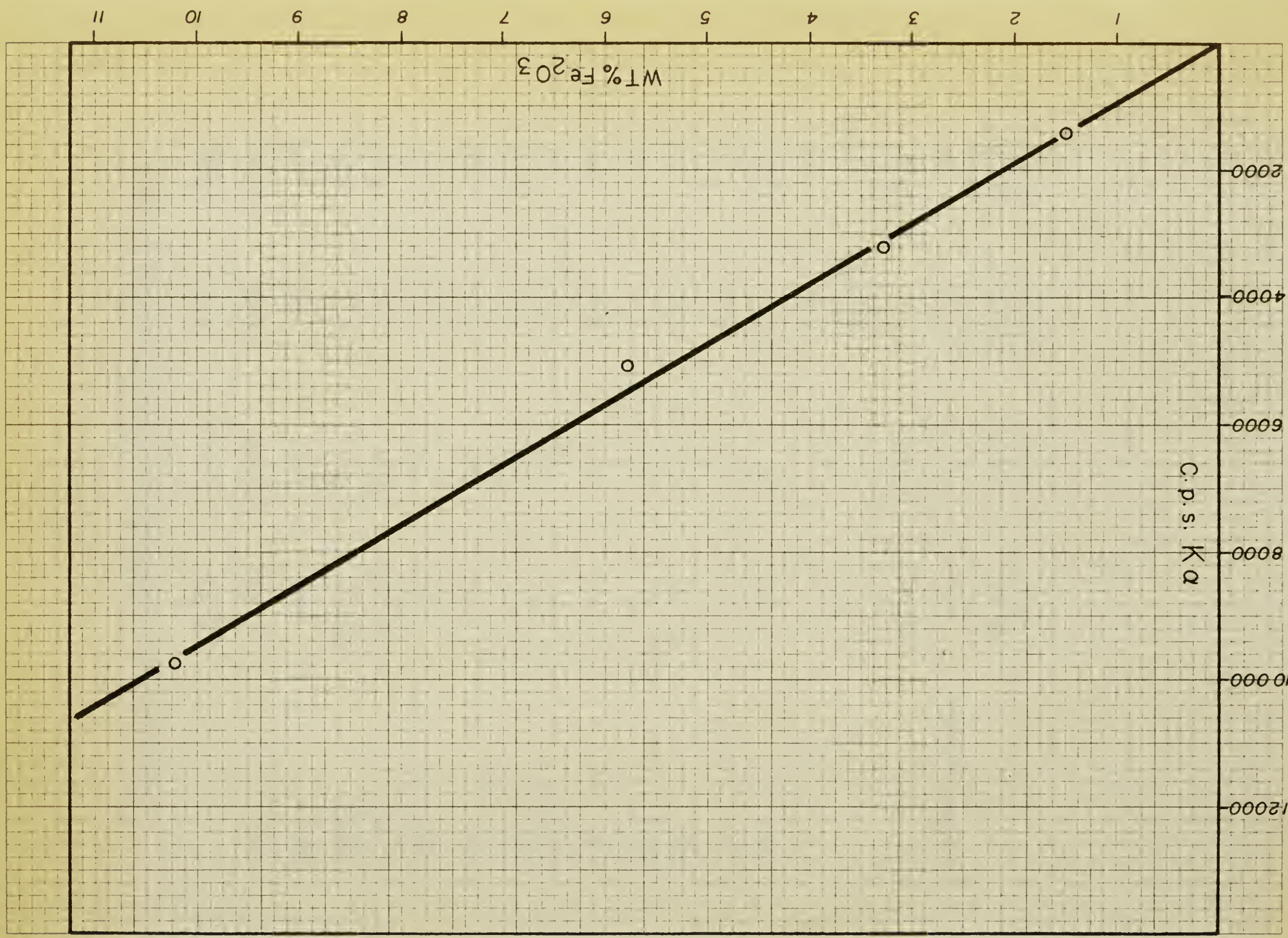

200
1000
800
600
400
200
C.p.s. Kα
10
20
30
40
50
60
70
80
90
WT. % SiO2
Uncorrected C.p.s.
C.p.s. corrected to common μ Si

XII



IIIX


5000
10000
15000
20000
C. p. s. Kα
0
2
4
6
8
10
12
14
16
WT.% CaO


WT% Fe2O3
1
2
3
4
5
6
7
8
9
10
11
2000
4000
6000
8000
10000
12000
C.p.s. Kα

Chemically Analysed Shale Standards Employed for Calibration Curves

	R 56	R 57	R 66	R 67
SiO_2	74.77%	53.65%	58.03%	54.26%
TiO_2	.60	1.08	.75	.28
Al_2O_3	10.27	18.18	17.31	5.55
Fe_2O_3	3.30	10.23	5.77	1.50
MnO	.02	.03	.01	.01
MgO	1.54	1.81	3.67	1.96
CaO	1.26	.59	.84	16.98
Na_2O	.44	.68	.71	.44
K_2O	2.00	3.76	2.24	.80
P_2O_5	.20	.27	.16	.07
H_2O^-	.78	1.70	1.55	.41
H_2O^+	2.96	6.25	5.27	1.69
CO_2	1.34	nil	nil	15.32
S	.68	1.62	1.30	.60
C			3.88 (?)	.44 (?)
	100.16	99.85	101.49	100.31
Less FeO as Fe_2O_3	.18	.35	.46	.11
	99.98%	99.50%	101.03%	100.20%

OPERATING CONDITIONS FOR X-RAY FLUORESCENCE ANALYSES

Element	Tube Type	Analysing Crystal	Peak Position	Background	Detector	Detector Voltage	Pulse Height Analyser Level	Window
Al	W	EDDT	142.79°	141.53°	Flow	1500	3	5.5
Si	W	EDDT	108.17°	106.57°	Flow	1500	4.5	5
S	W	EDDT	75.31°	76.16°	Flow	1500	6.5	5.5
K	W	EDDT	50.38°	49.73°	Flow	1480	6.5	7
Ca	W	EDDT	44.90°	45.82°	Flow	1500	3.5	15.5
Fe	W	LiF	57.53°	56.09°	Flow	1500	2	-
Mn	W	LiF	63.00°	61.02°	Flow	1500	5	-
Sr	Mo	LiF	25.12°	25.85°	Scint.	840	2	-
Rb	Mo	LiF	26.58°	26.05°	Scint.	840	2	-

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